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# TRANSLATION

MOTOR, JET, AND ROCKET FUELS

By

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FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

WRIGHT-PATTERSON AIR FORCE BASE

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# UNEDITED ROUGH DRAFT TRANSLATION

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BY: K. K. Papok, Ye. G. Semenido

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NOTE

The book "Motor and Jet Fuels and Rocket Propellants" is the fourth completely revised edition of the first volume of the book "Motor Fuels, Lubricants, and Liquids," issued in 1957.

This book examines in detail the physicochemical and operational properties of aviation, jet, rocket, automotive, diesel, and boiler fuels, as well as the basic problems relating to the qualities and utilization of these fuels in engines and aircraft assemblies and ground machinery. Individual chapters of the book are devoted to the most important problems in the area of fuels - corrosion and scale-formation properties, heat of combustion, low-temperature properties, tar formation, deposition, etc.

This book is intended for engineers and technicians working in areas in which fuels are used, as well as for those people engaged in the operation of various engines and the refining of petroleum.

## PREFACE TO THE FOURTH EDITION

The fourth edition of the book "Motor and Jet Fuels and Rocket Propellants" has been revised and changed so that it would probably best be referred to as a new book, rather than a new edition of the book published first in 1957.

Almost all of the chapters in this book have either been radically revised or rewritten entirely. Moreover, new chapters have been introduced.

This book contains the latest information on the quality and application of all types of jet, rocket, aviation, automotive, diesel, and marine fuels.

The part dealing with rocket propellants includes data published in foreign and Soviet literature.

## Chapter 1

## PETROLEUM

### THE IMPORTANCE OF PETROLEUM

Fuels and lubrication materials for aircraft, tanks, automobiles, tractors, seagoing vessels, etc., are derived primarily from petroleum.

Petroleum became one of the basic sources of energy because of its high heat of combustion. In the burning of 1 kg of petroleum approximately 10,600 kcal of heat are liberated on the average. For purposes of comparison let us point out that the burning of 1 kg of high-quality coal (anthracite) approximately 8,000 kcal are liberated, and in the burning of 1 kg of dry wood a total of about 4,700 kcal is evolved.

In the conversion of naval fleets from coal to petroleum, accomplished some 45 years ago, the power of the powerplants of fleets existing at that time (without counting the construction of new vessels) increased by one-third.

The invention, in 1880, of spray nozzles by Engineer V. G. Shukhov played an important role in the conversion of these ships to petroleum fuels; these spray nozzles made it possible to inject petroleum, in mixture with steam or air, into the boiler furnace.

The utilization of products from the refining of petroleum – fuels and lubricants for various purposes, and particularly motor fuels and lubricants – has been on the rise since the beginning of the present century. There were only four automobiles in the world in 1896, whereas by 1910 the number of automobiles exceeded 10 million.

During the Second World War approximately 40 million automobiles and tractors were in operation, there were some 150 thousand tanks, and more than 200 thousand aircraft. It is not difficult to conceive of the tremendous quantities of fuels and lubrication materials that all of this equipment required; without this material all of this equipment would have stood idle.

D.I. Mendeleyev, who had such great influence on the development of our domestic petroleum industry, pointed out that petroleum is a precious raw material for chemical refining.

During the past ten years, petroleum and natural petroleum gases have been employed in ever-increasing quantities as raw material for the chemical industry.

Petroleum is a complex mixture of carbon compounds and hydrogen - hydrocarbons - which make up the basic class in organic chemistry.

I.M. Gubkin, the outstanding Soviet scientist, developed the theory of the composite vegetable-animal origins of petroleum, widely employed in the search for new petroleum deposits.

According to this theory, remains of vegetation and animals, accumulated in bogs (in shallow seas, lagoons, and gulfs), act together with inorganic substances to form deposits which undergo continuous change when completely immersed in this section of the earth's crust for long periods of time, and as a result the sapropelic substances (the decaying mud) converts into petroleum.

The origins of the organic residues (for example, vegetative, or complex animal organisms, or the simplest of the single-celled creatures) in the final analysis determine the variety of products into which they will finally be converted, and this is one of the factors responsible for the existence of varieties of petroleum.

Temperature conditions within the rocks containing these residues also have an effect on the composition of the final transformation products, as does the catalytic effect of individual substances, in addition to the biochemical processes engendered by bacteria, geological changes within the rocks themselves, the action of radioactive elements, etc.

Petroleum contains some 84-87% carbon, and approximately 12-14% hydrogen. There are sulfur, oxygen, and nitrogen compounds in petroleum. The petroleum from a number of deposits (primarily from the regions of the Caspian and Black Seas) are poor in sulfur; the sulfur content rarely exceeds 0.3%. The petroleum from many of the deposits situated in the East of the country contain 2-3.5% of sulfur, and certain other deposits show figures reaching as high as 5%.

The nitrogen and oxygen content in petroleum varies from 0.4 to 1%, and rarely exceeds this value. These elements, as a rule, are found in combination with carbon and hydrogen.

Paraffinic (alkanes), naphthenic (cyclanes), and aromatic hydrocarbons are included in the composition of petroleum. Olefinic (alkenes) and diolefinic (alkadienes) hydrocarbons are rarely encountered in petroleum, but are formed in great quantities during the thermal treatment of the petroleum. In terms of its chemical composition petroleum is classified according to the predominance of hydrocarbons of certain classes, imparting specific properties to the petroleum, with these properties characteristic of the classes in question. The overwhelming majority of petroleum deposits are of the composite type: methane-naphthenic, naphthenic-aromatic, methane-aromatic, etc.

Of the paraffinic hydrocarbons (saturated, normal and isostructure) the majority of the representatives of this class, beginning with the simplest hydrocarbon, methane, are encountered in the composition of petroleum.

Of the naphthenic hydrocarbons (cyclic), designated in this manner by their discoverer, V.V. Markovnikov, the outstanding Russian chemist, the naphthenes whose closed cycles are formed predominately by five and six carbon atoms, i.e., the penta-and hexa-methylene series, are found in petroleum.

Aromatic hydrocarbons are encountered in petroleum both in the form of their simplest representatives (benzene, toluene) as well as in the form of more complex compounds.

By means of the basic reactions in organic chemistry: halogenation (the introduction of Cl, F, Br into the composition of the hydrocarbon molecule); nitration (the introduction of the nitrogroup $NO_2$); sulfonation (the introduction of the sulfur group $SO_2OH$); oxidation, etc., from the petroleum hydrocarbons their derivatives are obtained, and these are used either as semifinished products for subsequent synthesis or as finished products.

Nitration of paraffinic hydrocarbons, discovered by M.P. Konovalov, is used to obtain the nitroparaffins which are utilized as solvents for lacquers and paints as well as semifinished products for the synthesis of explosive materials, etc.

The nitration of aromatic hydrocarbons is employed to obtain such important nitrogen compounds as nitrobenzene which is reduced to aniline, trinitrotoluene (trotyl), and trinitrophenol (picric acid). The latter are powerful explosives; moreover, they are used as semifinished products for the synthesis of dyes.

Some of the most important products are obtained through the oxidation of the hydrocarbons. For example, the oxidation of ethylene is used to obtain ethylene oxide which is used for the production of synthetic rubber, artificial fibers, imitation leather, explosives, plastics, [illegible] and lubricant additives, etc.

Methyl alcohol is obtained by the oxidation of natural gas which consists primarily of methane. The incomplete oxidation of methyl alcohol is used for the production of formaldehyde which is used extensively in the production of phenol-formaldehyde resins as semifinished products for the production of various plastics.

Urotropine is obtained by combining formaldehyde with ammonia; urotropine was first synthezied by the founder of the theory of the chemical structure of organic compounds, A.M. Butler. Urotropine is used in the production of explosives, certain plastics, and as a medicinal preparation.

Products obtained in the chemical refining of petroleum and petroleum gases are used successfully in the place of products obtained from grain, potatoes, and other raw foodstuffs, such as are used in the production of synthetic rubber, detergents, consistent lubricants, etc.

The expansion in the production of synthetic plastics, and artificial fibers and fabrics is based primarily on products obtained through the chemical refining of petroleum and petroleum gas. For example, in order to obtain the well-known synthetic fiber caprone, we use the organic compound caprolactam ($C_5H_{10}CONH$), obtained from phenol, as the initial semifinished product.

For the synthetic fiber "lavsan" (terylene), the basic raw materials are the following: the aromatic hydrocarbon p-xylene, dibasic alcohol, ethylene glycol, and methyl alcohol. All of these initial materials are petroleum products.

The domestic petroleum industry – one of the basic ventures of heavy industry – underwent its greatest expansion after the Great October Socialist Revolution. During the years of Soviet power, the petroleum industry underwent complete technical reconstruction. A petroleum base area was set up in the eastern regions, between the Volga and the

Urals. Completely new plants have been built, and old plants were rebuilt, to handle the production of specific and required qualities of gasoline.

In 1960, 148 million tons of petroleum were produced. Simultaneously with this increase in the production of petroleum, the refining of petroleum is being expanded and intensified. New and improved industrial processes and methods for the production of fuels and lubricants are being introduced.

The 21st Congress of the CPSU established guide figures for the expansion of the national economy of the USSR for the period 1959-1965, and these called for high rates of development (expansion) in both the petroleum and gas industries. Particular attention was devoted here to the subsequent development of the eastern regions of the USSR.

The production of petroleum by 1965 is to reach a level of 230-240 million tons, i.e., an increase by a factor of 2 in comparison with the year 1958.

The petroleum refinery capacity must be increased during this period from 1959 to 1965: the capacity for the primary refining of petroleum must be increased by a factor of 2.2-2.3; the catalytic cracking capacity must be increased by a factor of 4.7; the catalytic reforming capacity must be increased by a factor of 16-18; and the production of lubricants must be increased by a factor of 2.

The planned volume of refining capacity will be completely adequate to cover the needs of the national economy with respect to petroleum products and will make possible substantial improvements in the quality and operational characteristics of automotive gasolines, diesel fuels, and lubricants.

The production of gas will show an increase by a factor of 5 in 1965, as opposed to 1958.

The plans call for the extensive development of production facilities for synthetic materials on the basis of gases obtained during the derivation of petroleum, natural gases, and the gases which are formed at the petroleum refineries.

During this seven-year plan, the production of artificial fibers will increase by a factor of 4; the production of plastics and synthetic resins will increase by a factor of more than 7.

THE HISTORY OF PETROLEUM

Petroleum is known to us from very ancient times. Archeological investigations have established the existence of petroleum and asphalt processing facilities as far back as the years 4000-6000 B.C.

For a long time, crude petroleum was gathered from natural surface pools, and later on it was extracted from shallow (up to 1-2 m deep) specially prepared pits (diggings). It goes without saying that only very small quantities of crude petroleum could be extracted by such technically imperfect methods.

From the middle of the 19th century, the demand for crude petroleum as a raw material for the production of "illuminating oils," increased sharply; these oils were used for purposes of lighting homes, industrial sites, and trade buildings, and these oils were also used for the production of lubricants. The utilization of a new and more progressive method of extracting petroleum by means of drilling through the earth's crust came into being.

Initially, the drilling depth for the extraction of petroleum involved only several hundreds of meters; at the present time, oilwells can be drilled to depths of 3000-6000 m and even deeper.

The demand for petroleum "illuminating oils" which resulted in the development of petroleum-extraction processes may be attributed to the fact that by the middle of the 19th century the advantages of these

products over the animal and vegetable fats used prior to this time for purposes of illumination became clearly evident. From that time on, the production of kerosene developed.

With the appearance of internal-combustion engines, and with the improvement of the latter, there arose a need for the most varied of fuel-lubrication materials and primarily for gasolines. The demand for these products is constantly on the increase. This provided a new incentive for the expansion of petroleum extraction and petroleum refining.

Many outstanding Russian and Soviet scientists and engineers worked and are continuing to work in areas of investigating and refining petroleum.

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## Chapter 2

## DATA ON THE PRODUCTION (TECHNOLOGY) OF LIQUID FUELS

The primary raw materials for the production of contemporary liquid fuels are petroleum, coal, shales, natural gases, and the gases which are formed in the refining of petroleum and in the processing of coal. In addition to direct distillation, there now exist on an industrial scale a number of thermal and catalytic processes for the refining of petroleum and these make it possible not only to produce liquid fuels but also make possible the control of these processes in order to obtain fuels of required quality. These methods are based on processes involving the transformation of the molecular structures of the hydrocarbons which serve to make up the initial raw material.

In addition to the purely synthetic processes of producing fuels, the processes involved in the refining of low-quality fuels (obtained either from petroleum or from synthetic fuels) into high-quality grades have come into widespread use, as have the processes involved in the production of specific groups of hydrocarbons or even individual hydrocarbons which provide for the high quality of liquid fuels.

### DERIVATION OF LIQUID FUELS FROM PETROLEUM

#### Direct Distillation

Individual fractions are extracted from petroleum (crude oil) in direct distillation by means of successive or simultaneous vaporization of these fractions, separating the vapors formed as a result and subsequently condensing these. This is the simplest and oldest method of petroleum refining.

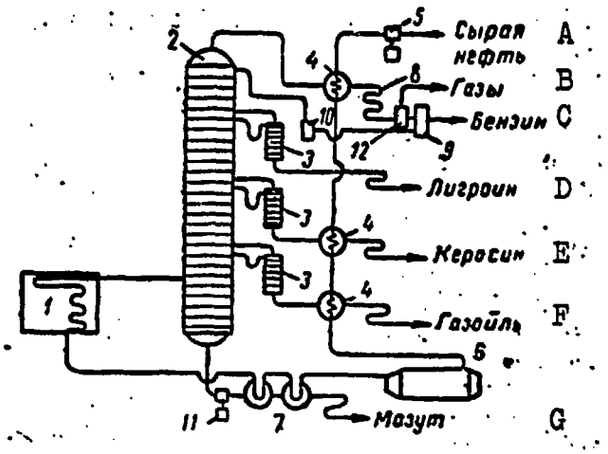


Fig. 1. Schematic arrangement of bubble-tray tower of a topping plant for the initial distillation of a crude oil. A) Oil; B) gases; C) gasoline; D) ligroin; E) kerosene; F) gas oil; G) mazout.

At the present time, bubble-tray towers of high capacity and great economy of operation are employed to carry out the direct distillation of the crude oil. The basic elements in these installations are the tube-still heater, in which the liquid portion of the petroleum is separated from the vapors that are formed, the rectification column and its auxiliary columns in which the vaporized portion of the crude oil is separated into individual fractions - the distillates; in addition, there are heat exchangers, condensers, receivers, pumps, etc.

There are a number of structural versions for direct-distillation installations: 1) with single vaporization of the entire portion to be distilled, in a single column; 2) with double vaporization of the portion to be distilled, in two successive columns; 3) with preliminary vaporization of low-boiling fractions in individual vaporizer, after heating of the crude in heat exchangers.

Figure 1 shows a schematic arrangement of an installation with

single vaporization. The petroleum is supplied under pressure through three distillation heat exchangers 4 by means of a centrifugal pump 5, and the petroleum is then continued through the decontaminator 6 and the oil heat exchangers 7 and, having been heated to 170–175°, the petroleum enters the tube-still heater 1. Heated to 330° in the tube-still heater and partially vaporized, the crude oil (petroleum) enters the rectification column 2 that has been fitted out with strippers 3. Gasoline and its side distillates – ligroin, kerosene, and gas oil – are removed in the column. The gasoline is withdrawn from the top of the column, and the side streams may be withdrawn through the strippers. The gasoline vapors are condensed and cooled in heat exchanger 4 and condenser 8. Passing through the gas separator 12, the gasoline enters receiver 9; a portion of the gasoline is withdrawn from the latter by means of pump 10 in order to flush the column. The side distillates, having passed through the heat exchangers and the condensers, are directed to the receivers. The mazout is pumped by means of pump 11 from the bottom of the column through heat exchanger 7 and the condenser to the receivers.

With direct distillation, liquid fuels are obtained only in such quantities as are actually present in the initial crude oil.

With the growth in aviation, automotive, and tractor equipment, the need for liquid fuel increased sharply and the quantities of fuel derived through the direct distillation of petroleum proved to be inadequate.

Approximately 30 years ago this led to the industrial development of processes for the derivation of gasoline from high-boiling petroleum products consisting of relatively large hydrocarbon molecules, said derivation accomplished by the splitting of these large molecules into the smaller hydrocarbon molecules of which gasolines are composed.

This process, taking place at high temperatures, was designated as the "cracking" process.

We distinguish between thermal and catalytic cracking. The latter is carried out at lower temperatures, but in the presence of catalysts.

Thermal Cracking

The final industrial execution of the thermal-cracking installation depends on the conditions of the process (temperature, pressure), the composition of the initial crude oil, and the purposes for which the final products are to be employed.

The various types of thermal-cracking installations existing at the present time can be reduced to three basic processes: 1) high-pressure cracking; 2) coking or cracking of the residuum at low pressure; 3) pyrolysis or high-temperature cracking at low pressure.

Formerly, typical crudes for thermal-cracking were the kerosene-gas-oil fractions, and the final product was gasoline. At the present time, low-grade heavy petroleum residues are subjected to cracking, and the final products, in addition to gasoline, include a wide fraction (which serves as the raw material for catalytic cracking) and a gas (which serves as raw material for chemical refining procedures).

Coking is carried out in order to obtain a lightened wide fraction (which is then subjected to the subsequent refining stage) and petroleum coke.

Various raw materials are subjected to pyrolysis in order to obtain a gas rich in unsaturated hydrocarbons (used for chemical processing), and aromatic hydrocarbons.

Heat causes the component hydrocarbons of the petroleum crude to undergo a number of changes. The trend and the extent of the reactions that take place in this case are defined by the conditions of the process and by the raw material itself. The basic process reaction i

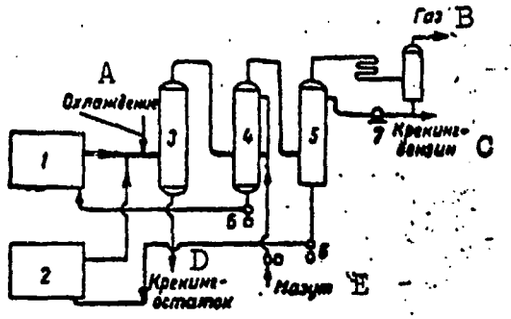


Fig. 2. Schematic arrangement of dual-tube (furnace) thermal-cracking installation. 1) Light-cracking furnace 2); deep-cracking furnace (tube); 3) vaporizer; 4) 1st column; 5) 2nd column; 6) hot-feed pumps; 7) flushing pumps; A) cooling; B) gas; C) cracking gasoline; D) cracking residue; E) mazout.

independent of the conditions - we refer here to the splitting of a more complex hydrocarbon molecule into a number of less complex molecules. As a result of this splitting reaction, gasoline and gases are obtained.

In the breaking up of the hydrocarbons, unsaturated molecules are formed. Therefore all gasolines and gases from the purely thermal processes contain unsaturated hydrocarbons; there are more unsaturated hydrocarbons in the high-temperature products than those produced by means of low-temperature processes.

With thermal-cracking consolidation and condensation of the split molecules take place, together with the formation of heavy residues and coke, as well as the reactions of aromatization, isomerization, etc. An increase in the pressure of the process enhances the consolidation reactions (polymerization, alkylation, etc.), and an increase in temperature enhances the reactions of splitting, condensation, and aromatization.

Raw materials having higher molecular weights (kerosene, gas oil

and mazout) are easily broken up at lower temperatures than are the lighter raw materials such as ligroin and especially gasoline. The latter two, in the case of thermal-cracking, show greater tendency to reactions of aromatization, dehydrogenation, and isomerization, which result in the formation of aromatic hydrocarbons, and unsaturated and isocompounds.

At the present time there exists a great quantity of various types of thermal-cracking installations.

Figure 2 shows the basic arrangement of a very common dual-tube (furnace) cracking installation which makes it possible to employ mazout as the initial raw material. The installation consists of a light-cracking furnace in which the initial mazout is subjected to cracking, and the installation further consists of a deep-cracking furnace in which the products of the mazout decomposition and the lighter fractions distilled from the mazout are subjected to cracking. The initial mazout is passed through a heat exchanger into one of the rectification columns where, encountering the vapors coming from the vaporizer, condenses the heavier portions of these vapors, and simultaneously the lightest fractions are vaporized from the mazout.

The mixture of the mazout residues and the heavy intermediate fractions are collected at the bottom of the column by means of a pump and passed into the light-cracking furnace. The derived light intermediate cracking fractions in mixture with the cracking-gasoline, the gas, and the solar distillate distilled from the mazout, are withdrawn from the top of the column and supplied to the second column, where the cracking-gasoline and gas fractions are separated from the remaining products. The latter are collected by means of a pump from the bottom of the column and fed to the deep-cracking furnace where the basic cracking process takes place. The cracking products from the two

furnaces are mixed and directed to the vaporizer. In the latter, the cracking products are separated from the cracking-residue which drips down into the vaporizer and is directed into the first column.

The temperature in the light-cracking furnace is 470-480° and in the deep-cracking furnace it is 500-510°. The pressure at the inlet to the first furnace is 40-45 atm and it is about 50 atm at the inlet to the second furnace.

The yield of cracking-gasolines may change within an extremely wide range (from 25-30% to 65-70%), depending on the raw material and the operating regime of the installation.

The cracking of light raw material – kerosene and gas oil – as well as of gasoline (for purposes of changing the chemical composition of the gasoline) is carried out in single-furnace cracking installations. In the cracking of gasolines, the process is carried out at a temperature of 550-560° and at a pressure of 20 atm.

Pyrolysis is a high-temperature cracking process (650-700° and higher) which takes place at atmospheric pressure. In the case of pyrolysis, in addition to the intensive breaking up of the original high-molecular hydrocarbons, there take place reactions involving the subsequent transformation of the products being split, and these result in the formation of aromatic hydrocarbons. However, the high gas yield in the case of pyrolysis (up to 50%), with this gas rich in unsaturated hydrocarbons, predetermined yet another purpose for pyrolysis, i.e., the production of a gas used for chemical processing.

Pyrolysis is carried out in retorts or gas generators. The primary raw material for pyrolysis is a kerosene distillate. Pyrolysis forms gas (up to 50%), tar (45-48%), carbon black, and coke (1-2%).

In the distillation process, 35-40% of light oil are separated from the tar (the fraction below 170°), and green pyrolysis oil (175-350° fraction); liquid pitch is formed in the residue.

The green pyrolysis oil is a product of little value and has no special application. The pitch is employed to obtain an ash-free coke.

The light oil enters the first rectification column and is separated into its fractions: the benzene head, and the benzene, toluene, and xylene fractions. The obtained fractions (with the exception of the benzene head) move on to the sulfuric-acid cleansing process, and then again to the rectification process for the derivation of pure aromatic hydrocarbons. The intermediate fractions, remaining after the separation of the aromatic hydrocarbons, are employed as components for liquid fuels. The separated aromatic hydrocarbons are used as components in aviation fuels or as raw materials for chemical processing. There exists another method for the processing of light oil, and here the individual aromatic hydrocarbons are not separated from the light oil, or only toluene is separated from the light oil. In this case, the light oil is separated from the benzene head and the remaining fractions; then the light oil is purified and released in the form of a mixture of aromatic hydrocarbons (up to 80-85%) with this mixture referred to as pyrobenzene.

The output of final aromatic hydrocarbons in pyrolysis is not great and does not exceed 15-20% of the raw material.

Catalytic Cracking

Catalytic cracking differs from thermal cracking in that the hydrocarbon vapors are the raw material being cracked or passed above a catalyst, i.e., a substance which accelerates and guides the course of the reaction. With the use of catalysts the temperature of the hydrocarbon decomposition drops and products quite unlike the thermal-cracking products in terms of quality are produced.

We know of a great many chemical compounds that are capable, to some extent, of acting as catalysts in the cracking process.

At the present time, aluminosilicates are the most common of th

catalysts for this process; these are conventional clays processed and enriched with admixtures of oxides of nickel, cobalt, copper, manganese, and other metals, or with special synthetic masses.

In the presence of these aluminosilicates, the breaking up of the hydrocarbons begins at 300-350° and takes place most intensely at 450-510°. The cracking is carried out at atmospheric pressure or at a small pressure of 2-3 atm. During the process, the catalyst is covered with carbon deposits and its activity diminishes. To restore the activity of the catalyst, the carbon deposits are periodically removed by flushing the catalyst with air at a temperature of 510°.

There exist three basic industrial catalytic-cracking methods, based on the utilization of an aluminosilicate catalyst: a) with a fixed catalyst; b) with a movable catalyst; c) with a powder "free-flowing" or pseudoliquified catalyst.

Cracking with fixed catalyst (Fig. 3).

In this process the catalyst is charged into the contact chambers in the form of a small-grain porous mass exhibiting high mechanical strength; varying quantities of vapors are the product to be subjected to cracking or passed through these contact chambers, as is the air for the regeneration of the catalyst. The operating cycle for the chamber consists in four operations: 1) the actual cracking (10 min.); 2) flushing with steam to remove the hydrocarbon vapors from the chamber (5 min.); 3) regeneration of catalyst (10 min.); 4) flushing with steam to remove products of combustion from chamber (5 min.). Consequently, the entire cycle is completed within 30 minutes.

In order to provide for continuous operation of the installation, 3-6 chambers operating in series and switched automatically, are set up because each of the chambers functions only periodically.

The reaction chambers are cylindrical columns that are 11 m high, 3 m in diameter, and each equipped with three series of tubes.

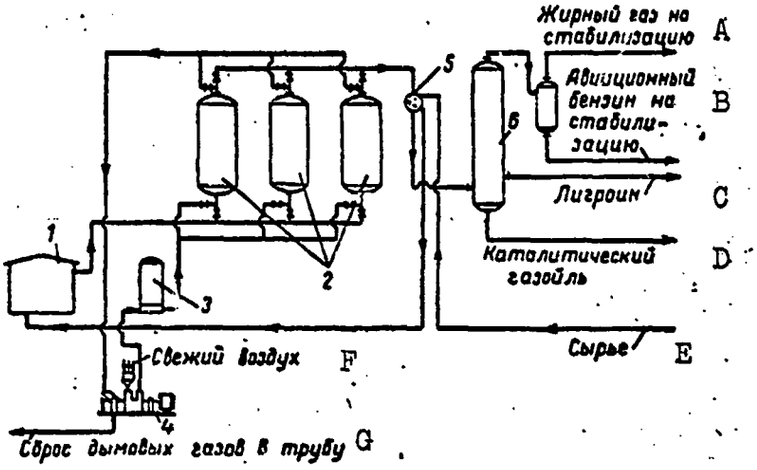


Fig. 3. Schematic arrangement of catalytic cracking installation with fixed catalysts. 1) Tube-still heater; 2) reactors; 3) air heater; 4) turbine compressor; 5) heat exchanger; 6) rectification column; A) fatty gas for stabilization; B) aviation gas for stabilization; C) ligroin; D) catalytic gas oil; E) charge; F) fresh air; G) flue gas.

The catalyst is placed in the space between the tubes. The first series (bank) of tubes is used to supply the vapors of the raw material to be subjected to cracking, as well as to carry the air and steam; the second bank is employed for the removal of the cracking products, the products of coke combustion in the regeneration of the catalyst, as well as the excess air and steam employed in the flushing process; the third series of tubes is employed for the circulation of the fused salts which remove the heat of regeneration and maintain the temperature during the cracking process.

The raw material (charge) for cracking generally consists of kerosene, gas oil, and solar fractions.

The catalytic-cracking products can be used both as automotive and aviation gasolines. To produce aviation gasoline, the cracking is done in two stages. The products of the first stage, which boil below 210-220°, are again passed through at a temperature of 400-450° over the catalyst and subjected here to catalytic purification.

The basic cracking process takes place during this first stage, and here the gasoline containing a comparatively large percentage of unsaturated hydrocarbons is formed. During the second stage, these hydrocarbons are subjected to isomerization, cyclization, and hydrogenation, as a result of which the gasoline is enriched with isoparaffinic and aromatic hydrocarbons.

The yield of aviation gasoline from the two-stage process amounts to 25-28%. The yield of automotive gasoline from the single-stage process amounts to 40-45%.

In addition to gasoline, the catalytic cracking process forms 15-21% gas, 40-50% gas oil, and 5-7% carbon deposits.

Unlike thermal cracking, no such valueless product as cracking residue is formed during the catalytic process.

In the catalytic cracking gases there are 35-40% unsaturated hydrocarbons (of these, up to 20% are butylenes), as well as up to 25-30% isobutane. Therefore catalytic-cracking gases serve as valuable raw material for the production of the high-octane aviation-gasoline component - "alkylate."

Cracking with movable catalyst (Fig. 4)

Natural clay (aluminosilicate) in the form of grains (pellets), or a synthetic "bead" catalyst with spheres having a diameter of about 3.5 mm, are used as the catalyst for this process. The "bead" catalyst is now being used predominantly.

The process involves the passage of the vapors from the product being cracked into a reaction chamber through a catalyst moving toward these vapors. A number of baffles have been installed in the reaction chamber, and these are intended to provide for a closer and longer contact between the vapors of the petroleum product and the catalyst. The vapors enter from the bottom and are removed from the

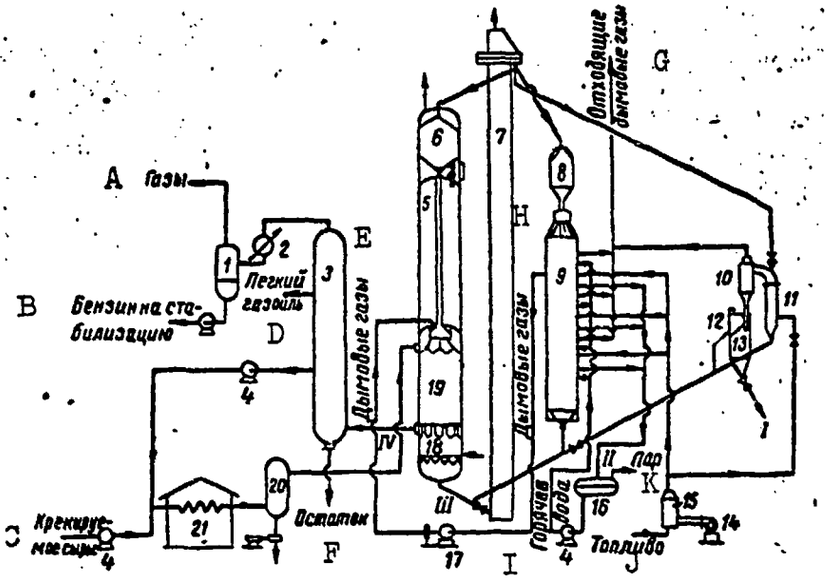


Fig. 4. Schematic arrangement of catalytic-cracking installation with movable catalyst. 1) Gas separators; 2) condenser; 3) rectification column; 4) pump; 5) frame for descent of catalysts; 6) catalyst hopper; 7) elevator; 8) regenerator hopper; 9) regenerator; 10) cyclone separator; 11) device for removal of dust; 12) hopper for fresh catalyst; 13) hopper for catalyst fines; 14) air blower; 15) flue-gas regenerator; 16) vapor separator; 17) turbine compressor; 18) distributor grids for catalyst; 19) reactors; 20) vaporizer; 21) tube-still heater;
LINES: I) removal (descent) of catalyst dust; II) vapor-mixture feed; III) removable (descent) of spent catalyst; IV) products-of-reaction feed: A) gases; B) gasoline for stabilization; C) cracking charge; D) light gas oil; E) flue gases; F) residue; G) outgoing flue gases; H) flue gases; I) hot water; J) fuel; K) vapor.

top of the chamber, whereas the catalyst, conversely, moves freely from its hopper and enters from the top of the chamber and is removed at the bottom of the chamber. The spent catalyst leaves the chamber by means of a scoop conveyor and is taken to the top of the regenerator where it passes through a series of successive zones before reaching the hot air. The regenerated catalyst is taken from the bottom of the re[illegible]

tor in a second scoop conveyor which carries the catalyst back to the hopper.

There are several structural versions of a cracking installation involving the use of a movable catalyst.

The process is conducted at a temperature ranging from 480 to 500° and at a pressure between 0.7 and 1.1 atm. With the "bead" synthetic catalyst the yield of aviation gasoline reaches 30-50%, by volume, and the yield of automotive gasoline attains 40-65%, by volume. Aviation gasoline, as in the case of cracking with a fixed catalyst, is produced in two stages.

Cracking with a pseudoliquefied catalyst

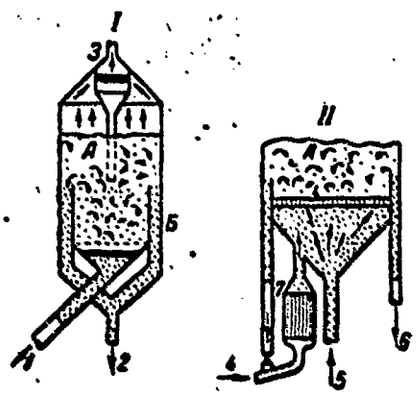


Fig. 5. Schematic arrangement of reactor and regenerator, with pseudoliquified (fluid) catalyst. I) Reactor; II) bottom of regenerator; A) pseudoliquified catalyst (boiling layer); B) stripper (annular) section; 1) inlet for charge and catalyst; 2) outlet for spent catalyst; 3) outlet for products of reactions; 4) air inlet; 5) inlet for air and catalyst; 6) outlet for regenerated catalyst; 7) condenser.

The catalyst in this process (natural clays or a synthetic aluminosilicate catalyst ground down to a fine dust with a particle dimension of 300 mesh or lower) is introduced into a stream of a charge that has been vaporized in advance and this stream is directed to the reactor. The catalyst is carried through the reaction chamber by the stream of vapors and gases. The spent catalyst is removed from the vapors and enters the regenerator where it is picked up by hot air which burns off the carbon-like deposits from the catalyst surface. The catalyst enters the cyclone separator from the regenerator together with the flue gases, and it separates from the flue gases in the cyclone separator and again enters the reactor.

In newer installations, the catalyst is continuously introduced into the vapor streams and mixed with these vapors it enters the lower part of the reactor where a definite catalyst level is maintained. The spent catalyst is continuously removed for regeneration from the bottom of the reactor (Fig. 5).

One feature of the structurally improved new so-called orthoflow-process installation is the fact that both the reactor and the regenerator have been consolidated into a single combined piece of equipment and are positioned one above the other, with the lines carrying the catalysts and connecting the reactor to the regenerator situated on the inside.

The temperature of the process ranges from 450-480° and the pressure varies from 0.8-1.6 atm.

For this process, high-boiling products all the way to mazout can be employed as the charge, as can coking products which boil off within a range from 220-545°, and the gas oils of catalytic cracking.

The yield in cracking products and their quality corresponds approximately to the yields for cracking with a movable catalyst (the moving-bed catalytic process).

DERIVATION OF LIQUID FUELS FROM COAL

There are three basic means of processing coals into liquid fuels: coking and semicoking, hydrogenation, and the production of water gas which serves as the base for the subsequent synthesis of fuels.

In the case of coking and semicoking, we obtain products which are primarily subjected to hydrogenation.

Hydrogenation. Various coals, as well as coking and semicoking tars are subjected to hydrogenation. The process takes place at a high temperature (380-550°), and at a high hydrogen pressure (200-700 atm) in the presence of special catalysts.

The hydrogenation process is carried out in three stages. During the first stage, the process takes place in the liquid phase in the presence of a catalyst which contains an oxide of iron. Here a wide fraction is obtained, which then enters into the second hydrogenation stage which takes place at a temperature ranging from 390-440° and at a pressure of 200-300 atm above the tungsten sulfide deposited on a special carrier.

The hydrogenation products of the second stage are fractionated, with withdrawal of the gasoline fraction that is used as automotive gasoline.

After the removal of the automotive gasoline, the residue which begins to boil at 200° enters the third hydrogenation stage which employs the same catalyst and takes place at 360-450° and at a pressure of 230-300 atm. After the fractionation of the hydrogenation products, aviation gasoline is obtained.

New catalysts have recently been developed: a cobalt-molybdenum catalyst on an aluminum-oxide base, and a nickel catalyst on an aluminosilicate base, which make it possible to carry out the hydrogenation process at a lower pressure (below 125 atm) and to obtain gasolines with higher antiknock properties.

Derivation of liquid fuels from water gas. Water gas is a mixture of carbon dioxide and hydrogen in a 1:2 ratio. Water gas is obtained by passing steam through hot coals. Any type of coal, beginning with lignite and ending with coke, may be used for this purpose. The process is executed in gas generators.

The synthesis of hydrocarbons from water gas takes place over a colbalt-magnesium or an iron catalyst under a pressure of up to 15 atm and at a temperature below 200°.

## PROCESSES TO IMPROVE THE QUALITY OF THE BASE GASOLINES

### Catalytic Reforming in the Presence of Hydrogen (Hydroforming)

The catalytic reforming process is intended for the improvement of the antiknock properties of gasolines and ligroins by transforming six-member naphthenic and paraffinic hydrocarbons into aromatic hydrocarbons. In addition, the isomerization of five-member naphthenic hydrocarbons into six-member hydrocarbons and paraffinic hydrocarbons into isoparaffinic hydrocarbons.

The process involves the passage of raw-material vapors at temperatures ranging from 455 to 537° and pressures ranging from 7 to 50 atm in a hydrogen atmosphere or in the atmosphere of a gas rich in hydrogen through the catalyst.

The utilization of hydrogen in the process counteracts the intensive formation of coke. It is for this reason that the catalyst can be used for a long period of time without regeneration.

A great many varieties of catalytic reforming processes have been worked out, and these differ from one another in terms of installation structure and the nature of the catalyst employed.

Catalytic reforming is carried out primarily with two catalysts: a platinum catalyst and one based on molybdenum. In addition cobalt-molybdenum and chrome catalysts are used. The platinum catalyst, to a greater extent than the molybdenum catalyst, promotes the isomerization reactions of normal paraffinic hydrocarbons and the conversion of five-member naphthenic hydrocarbons into six-member hydrocarbons. With the platinum catalyst there is less destruction of the paraffinic hydrocarbons and the formation of coke is reduced to the minimum. Therefore, a platinum catalyst can be employed for a long period of time without regeneration and provides for greater yields of gasoline with better antiknock properties. However, this catalyst is easily poisoned by

sulfur compounds.

Reforming with a platinum catalyst is carried out in a fixed layer of a reactor system. Existing installations can be divided into three groups on the basis of the processes which these installations carry out: a) without catalyst regeneration (platforming); b) with intermittent regeneration of the catalyst, this step carried out whenever necessary as, for example, as a consequence of the disruption of the regime ("catforming," and Houdry forming); c) with periodic regeneration of catalyst.

The platforming process takes place in the following regime: the temperature range is between 455 and 482°, the pressure is below 50 atm, and the molecular ratio between the hydrogen and the raw material is 10:1. Platinum, in a quantity of 0.1-1.0%, is applied to the activated aluminum oxide.

During the "catforming" process, the regeneration of the catalyst takes place directly within the reactor. The catalyst is a combination of the hydrogenating component (platinum) and the cracking component - aluminum acid silicate. "Catforming" is carried out at a pressure of 33-35 atm. During the Houdry forming process, a dual-function catalyst is employed: this catalyst exhibits great selectivity and is intended to accelerate the reactions taking place during the reforming. The temperature of the process ranges between 465 and 510°, and the pressure is 20 atm.

As a result of periodic regeneration of the platinum catalyst, the process can be conducted at a somewhat lower pressure (13-20 atm), and this enhances the dehydrogenation reactions in which the aromatic hydrocarbons are formed.

Reforming with molybdenum catalyst is carried out not only in a fixed layer in reactors, but with moving caked or pseudoliquefied

catalysts. Reforming in the fixed layer above the molybdenum-oxide catalyst applied to the aluminum oxide was the first catalytic reforming process, and became well known as "hydroforming." Hydroforming is carried out at 537° and at a pressure between 20 and 35 atm.

Reforming with a moving catalyst, or "hyperforming" is carried out over cobalt molybdate at 425-482° and 27 atm. The catalyst moves very slowly in a continuous layer through the reactor downward under the force of gravity and returns to the top of the reactor by means of a pneumatic elevator; the regeneration of the catalyst takes place simultaneously with the movement of the catalyst upward through the catalyst lines. In the present of cobalt molybdate, simultaneously with the dehydrogenation of the naphthenic hydrocarbons into aromatic hydrocarbons, the hydrogenation of the unsaturated hydrocarbons and desulfurization take place. This makes it possible to subject not only direct-distilled gasolines but mixtures of these with cracking gasolines and high-sulfur-content products to reforming.

There are two designs of catalytic-reforming installations with pseudoliquefied catalysts (molybdenum oxide and aluminum oxide); the reactor and regenerator are situated on one level and the regenerator is positioned above the reactor ("orthoforming"). The utilization of the process with pseudoliquefied catalysts makes it possible to increase the final-product yield, to improve its quality, and to employ higher-boiling products as raw material than is the case in "hydroforming" (all the way to kerosene). In the case of catalytic reforming with a chrome catalyst, a moving pellet catalyst is employed, i.e., synthetic aluminochrome gel which at a low hydrogen pressure (7-14 gage pressure) and a temperature of 510° provides for a high degree of desulfurization and is easily regenerated at lower temperatures than is the case with the cracking catalyst. Because of these catalyst prope-

ties it becomes possible to process various types of raw material, whether high in sulfur content or products of thermal cracking.

Gasoline fractions boiling off within a range from 80-180°, and in certain cases ligroin and even kerosene are generally subjected to catalytic reforming.

Isomerization

Isomerization is employed for the pentane and hexane fractions, which are removed from the catalytic-reforming gasoline. The purpose of isomerization is to convert normal pentane and hexane, as well as hexanes with a single methyl group into more branched hydrocarbons, exhibiting higher antiknock properties. At the present time, there are three various processes of isomerization; these processes are designated commercially as follows: "isomat," "penex," and "pentafining." In the "isomat" process the aluminum-chloride hydrocarbon complex is activated by anhydrous hydrogen chloride, and this is supplied into the reactor in countercurrent to the charge. Isomerization takes place in the liquid phase at 120° and at a hydrogen pressure of 50-55 gage pressure.

The "penex" process is carried out with a platinum unregenerated catalyst in the presence of hydrogen. In the "pentafining" process, a special isomerization catalyst is employed; this catalyst is a combination of platinum, silicon, and aluminum oxide. The "pentafining" process takes place at a temperature of 426-482°, and the hydrogen pressure ranges from 20 to 40 atm. The catalyst is periodically regenerated. In both of these processes the catalyst is fixed.

PURIFICATION OF THE BASE GASOLINES

Both direct-distillation gasolines and those gasolines produced by secondary refining methods must be purified in the majority of cases in order to reduce the acidity and to remove the sulfur compounds, i.e., primarily hydrogen sulfide and the mercaptans.

To reduce gasoline acidity, alkali purification is employed. The latter is carried out on various types of equipment, i.e., mixers, columns, and agitaters. Alkali purification is used also to remove hydrogen sulfide. Here the mercaptans – primarily the lower – are also partially removed.

The thermal-cracking gasolines are treated with Fuller's earth in the vapor phase in order to remove unstable compounds.

Hydraulic purification, carried out either in the vapor or liquid phase, * is the best method for thorough desulfurization.

Vapor-phase hydraulic purification is carried out over tungsten-nickel-sulfide at a pressure of 52.5 gage pressure. The temperature is a function of the fractional composition of the raw material, the desired extent of desulfurization, and the activity of the catalyst, and ranges between 230 and 370°. The catalyst is regenerated after a period of 2 to 4 months in the case of thermal or catalytic cracking, and after 10 months in the case of the direct distillation of the crude. The yield of purified product attains 100% by volume.

The reduction in the mercaptan content in the gasolines is either accomplished by removing these, or by means of oxidation into less active compounds – disulfides.

The mercaptans are removed with a 43% alkali solution at 50-55° or at standard temperature in the presence of salts of acid oils, capable of dissolving the mercaptans into alkalis. To achieve this same effect, small quantities of tannin or propionic and butyric acids or alkylphenols are added to the caustic potash solution.

For the oxidation of the mercaptans into disulfides, the gasolines are treated with a sulfur-test solution, hypochlorite, sulfuric acid, 12% solution of caustic soda, containing 35 g/l of the decahydrate of sodium ferrocyanide, and a number of other methods are also employed.

DERIVATION OF GASOLINE COMPONENTS

Such high requirements are imposed on the quality of aviation fuels and certain grades of automotive gasolines that it is, as a rule, impossible for direct-distillation gasolines and catalytic gasolines from the refining of products obtained from petroleum or coal to satisfy these requirements, and this is all the more true of the liquid fuels produced synthetically. Therefore in order to obtain fuels of the required quality, depending on the initial properties of the above-enumerated base gasolines, either special high-quality components are added to these base gasolines, or their quality is improved by subjecting the hydrocarbons making up these gasolines to some chemical transformations.

Aromatic and paraffinic hydrocarbons having structures which provide for high quality serve as components for aviation fuels and the highest-quality automotive gasolines. The majority of these components (alkylates, industrial isooctane, alkylbenzen, etc.) are presently being derived from thermal- and catalytic-cracking gases, as well as through catalytic reforming in the presence of hydrogen, and also through pyrolysis, in addition to being derived from natural gases.

Finally, in order to obtain certain aromatic components, the pyrolysis of kerosenes is employed.

Below we present some brief data and basic schematic-industrial flow charts of the processes used to obtain various components.

Polymerization and Hydrogenation

In the case of polymerization, two or several molecules of unsaturated hydrocarbons are combined into a single more complex molecule.

The purpose of the polymerization process is to obtain liquid fuels or fuel components from cracking and pyrolysis gases, as well as from the gases produced in the various catalytic processes employed for the

refining of petroleum and coal products.

Only unsaturated hydrocarbons enter into the polymerization reaction: ethylene, propylene, the butylenes, isobutylene, and amylenes, if the latter are contained in the cracking gas.

The polymerization of the above-enumerated hydrocarbons is carried out by either the thermal (high temperatures and pressures) or catalytic methods.

Catalytic polymerization is being used extensively at the present time; the raw material for this method is exclusively the butylene fraction of a gas consisting of butylenes and isobutylene (selective polymerization). In the polymerization of such a raw material, primarily a mixture of isooctylenes is formed. During polymerization, both side products of reaction and unsaturated hydrocarbons are formed.

After the hydrogenation of the polymerization products, industrial isooctane is obtained, and this is a high-octane component of gasolines.

Selective catalytic polymerization is carried out in the presence of sulfuric or phosphoric acid.

Alkylation

By "alkylation" we mean the replacement of hydrogen in any organic compound of the alkyl group ($CH_3-$, $C_2H_5-$, $C_3H_7-$, etc.). In petroleum engineering, the alkylation reactions that are associated with joining of the unsaturated-hydrocarbon molecule to the isoparaffinic or aromatic hydrocarbon molecule found application, and this resulted in the formation of a product that was saturated in character. The alkylation process is employed to obtain high-quality aviation-fuel components.

There are two basic types of alkylation processes: thermal and catalytic.

Catalytic alkylation found greater application than did thermal alkylation. Isobutane and benzene are subjected to catalytic alkylatio

and as a result we obtain products that are either paraffinic or aromatic in nature.

Alkylation of isobutane

The catalytic alkylation of isobutane takes place in the presence of sulfuric or phosphoric acid, or in the presence of aluminum chloride.

Sulfuric-acid alkylation (Fig. 6) is employed primarily for the alkylation of isobutane with iso- and n-butylenes .

In the alkylation of isobutane with butylenes, the basic reaction product is a mixture of isooctanes: 2,2,3-trimethylpentane and 2,2,4-trimethylpentane.

In addition, the sulfuric acid results in a number of side reactions as a result of which paraffinic hydrocarbons of both higher and lower molecular weight than the isooctanes are produced.

The mixture of the paraffinic hydrocarbons – the products of the alkylation of isobutane with butylenes – has been designated as an alkylate.

The conditions for the alkylation process have a substantial effect on the yield and quality of the final alkylate. The optimum relationship is 5-6 moles of isobutane per 1 mole of unsaturated hydrocarbons.

In the presence of hydrofluoric acid, unlike sulfuric-acid alkylation, isobutane is as easily alkylated with propylene, butylenes, and amylenes. The introduction of propylene into the process of alkylation approximately doubles the raw-material reserve.

Hydrofluoric-acid alkylation takes place at room temperature. For alkylation, 100% hydrofluoric acid is used; the molar ratio of the isobutane to the unsaturated hydrocarbons varies from 3:1 to 1.5:1.

In the presence of aluminum chloride, the alkylation of isobutane is carried out with ethylene and propylene.

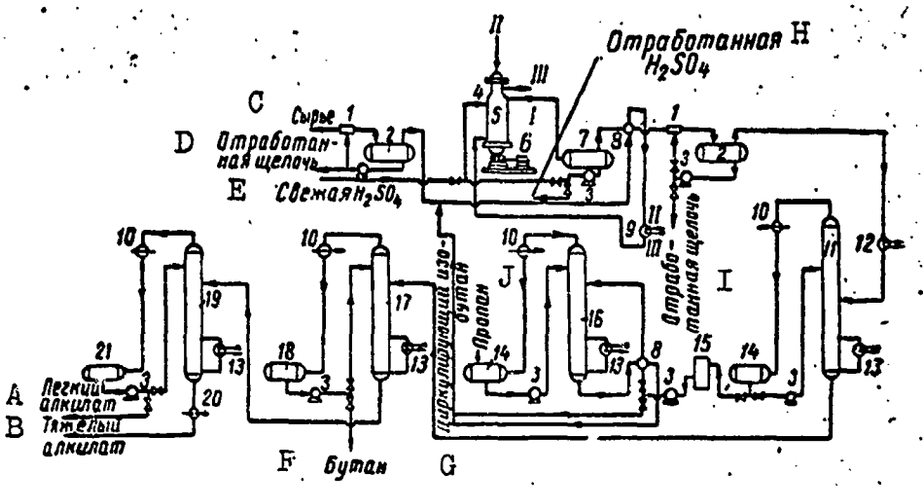


Fig. 6. Schematic arrangement of sulfuric-acid alkylation of isobutane. 1) Alkali mixer; 2) alkali settler; 3) pumps; 4) acid inlet; 5) contactor reactor; 6) mechanism for rotation of small lever in contactor; 7) sulfuric-acid settler; 8) heat exchanger; 9) ammonia cooler; 10) condenser; 11) de-isobutanizer; 12) heater; 13) boiler; 14) accumulator; 15) collector for circulating isobutane; 16) depropanizer; 17) debutanizer; 18) butane accumulator; 19) alkylate rectification column; 20) coolers; 21) light alkylate accumulator; Lines: I) alkylation product yield; II) ammonia inlet; III) ammonia outlet; A) light alkylate; B) heavy alkylate; C) charge; D) spent alkali; E) fresh $H_2SO_4$; F) butane; G) circulating isobutane; H) spent $H_2SO_4$; I) spent alkali; J) propane

Alkylation of benzene

Sulfuric, phosphoric, and hydrofluoric acids as well as a boron-fluoride catalyst are employed as catalysts for the alkylation of benzene.

The conditions for the process are governed by the catalyst employed.

In the case of sulfuric-acid alkylation, with 96% sulfuric acid, the process takes place at 0-15° and at atmospheric pressure. The same conditions prevail for the reaction in the presence of hydrogen flouride.

When working with phosphoric acid, we find that the temperature of the reaction varies between 180-240°, and the pressure lies in an

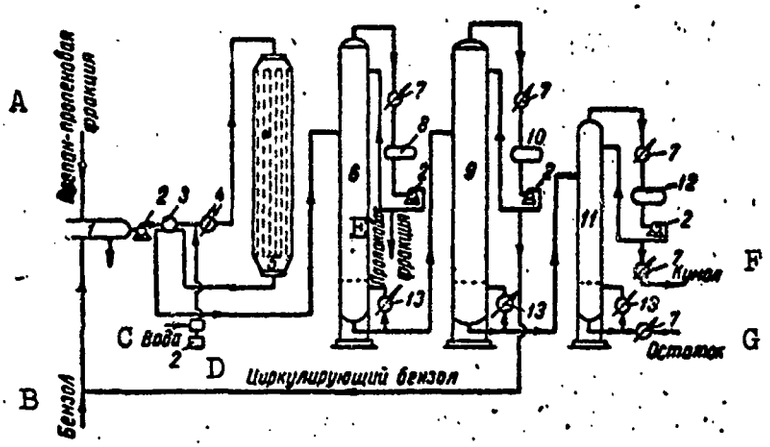


Fig. 7. Schematic arrangement of phosphoric-acid alkylation of benzene. 1) Accumulator; 2) pump; 3) heat exchanger; 4) vaporizer; 5) reactors (only one shown); 6) depropanizer; 7) water cooler; 8) propane accumulator; 9) column for separation of benzene; 10) benzene accumulator; 11) column for separation of isopropylbenzene; 12) isopropylbenzene accumulator; 13) hot-oil boiler; A) propane-propenen fraction; B) benzene; C) water; D) circulating benzene; E) propane fraction; F) cumene; G) residue

interval between 15 and 30 atm.

For alkylation we use gases from cracking or pyrolysis, these gases containing either the unsaturated hydrocarbons from ethylene to butylene, depending on the production conditions, or a mixture of ethylene with propylene or a mixture of propylene with butylenes, or, finally, ethylene, propylene, or butylenes - each separately. Figure 7 shows a diagram of a phosphoric-acid installation for the alkylation of benzene with propylene.

DERIVATION OF JET AND DIESEL FUELS

Jet and diesel fuels are obtained primarily through the direct distillation of petroleum. However, the quantities of catatylic-cracking products employed as diesel fuels increases each year. Thermal-cracking products are also finding application as components for jet

and, partially, for diesel fuels.

In the production of jet and, particularly, of diesel fuels from paraffinic and sulfur-bearing petroleums, it becomes necessary to devise special methods for the processing and purification of these fuels. Thermal-cracking products are subjected to purification, as are the highly aromatized catalytic-cracking products.

The direct distillation products obtained from paraffinic petroleums are subjected to deparaffinization which can be carried out in either of two ways – the destructive freezing of high-melting paraffinic hydrocarbons in the presence of solvents, with the subsequent filtering of the fuels; and the improved carbamide method which has come into industrial use in recent years. This method is based on the capacity of carbamide to form solid complex compounds with the paraffinic hydrocarbons contained in the distillates of jet and diesel fuels at ordinary temperature. The formed complexes are easily separated, as a result of which it becomes possible to obtain a fuel with a low pour point without the use of expensive cooling methods. Generally, a methanol solution of carbamide is used.

In the diesel fuels obtained from sulfur-bearing petroleums, the sulfur content attains 1.0-1.2%, and in certain cases even 1.5-1.6%. The successful desulfurization of such fuels can be accomplished only through catalytic hydraulic purification which is accomplished by the introduction of hydrogen from the outside (actually hydraulic purification), and by employing the hydrogen which is generated in the dehydrogenation of the naphthenic hydrocarbons contained in the crude (autchydraulic purification).

There are several versions of the hydraulic purification process, each differing from the other in the equipment employed. The hydraulic purification process is generally carried out with a fixed alumino-

cobalt-molybdenum catalyst contained in the reactor at a pressure ranging from 10 to 70 atm (most frequently at 40-50 atm) and at a temperature ranging between 390 and 420°. Under these conditions, the destructive hydrogenation of the sulfur compounds takes place, with the formation of hydrogen sulfide; under these conditions the unsaturated hydrocarbons also experience hydrogenation, as do the oxygen- and nitrogen-bearing compounds. Hydraulic purification provides for a 95-98% degree of fuel desulfurization.

The process of autohydraulic purification is carried out with the same catalyst, but at a lower hydrogen pressure (5-15 atm); therefore, it becomes possible to carry out the dehydrogenation of the naphthenic hydrocarbons at a temperature of 400° and higher. Autohydraulic purification is used only for a raw material enriched with six-member naphthenic hydrocarbons which serve as sources for the derivation of the hydrogen. Therefore, this process is primarily carried out on a direct-distillation crude or mixtures of this raw material with cracking products. The desulfurization of diesel fuels amounts to 50-85%, and of the gasoline-ligroin fractions amounts to 95-97%.

[Footnote]

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30 The process in the liquid phase will be characterized in the examination of the method used to obtain diesel and jet fuels for which this process is most typical.

## Chapter 3

## EVALUATION OF PHYSICOCHEMICAL PROPERTIES OF FUELS

The GOST for a fuel lists more than 15 different indices from which we may draw inferences as to its properties.

Some of these indices may be used to obtain an idea of the fuel's operational properties, i.e., a conception of how the fuel in question will behave on combustion in an engine, how it will foul the engine with tarry products, whether it will cause corrosion of the engine and tank components, the extent to which starting of the engine will be made more difficult or easier, and so forth. Other indices serve to characterize the chemical composition of the fuel and its component parts and, consequently, express the operational properties of the fuel only indirectly.

There are a number of indices that are used chiefly to check the identity of fuel consignments; in determining the chemical nature of a fuel, such indices are useful only in combination with others.

Each of the numerous indicators is important in itself, but only the combination of all of them provides a complete conception as to the properties of a given fuel.

These indices are extensively used in the following cases: in quality control of the fuel in production, in operation, in research work and in development of new types of fuel, and in study of the changes that take place in the properties of fuels under the conditions of storage, shipping, and use.

In using the indices, it is extremely important to know exactly

what the index in question represents, the numerical units and the precision with which it is determined, how it is related to other indices and what operational properties of the fuel can be evaluated using it as a basis.

It is from this viewpoint that the present chapter considers all of the physicochemical indices used to evaluate fuel quality, with the exception of octane number, grade and cetane number, which, in view of the specific points to be observed in their determination, are analyzed in the chapter on evaluation of the detonation resistance of fuels.

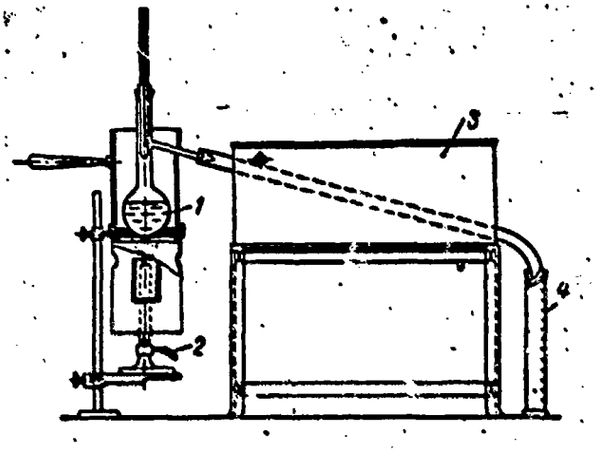



Fig. 8. Diagram of standard apparatus for distillation of liquid fuels. 1) Flask; 2) burner; 3) condenser; 4) receiver.

## VAPORIZABILITY

The vaporizability of a fuel is judged primarily from its fractional composition and vapor pressure, or, in other words, on the basis of the fuel's saturation vapor pressure.

### Fractional Composition

The fractional composition of a fuel is determined on a standard apparatus in accordance with GOST 2177-48 (Fig. 8). Essentially, the test reduces to splitting the fuel into individual fractions. A 100-ml sample of the fuel is poured into an Engler flask and heated. Passing

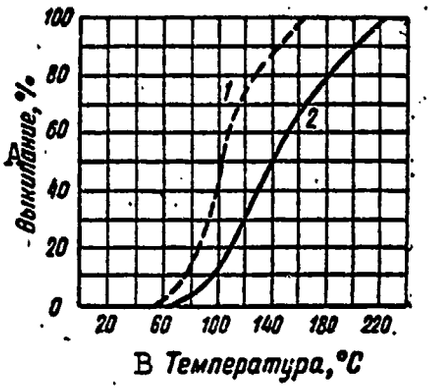



Fig. 9. Distillation curves of fuels. 1) Aviation gasoline; 2) automobile gasoline. A) Percentage boiled out; B) Temperature, °C.

through the escape tube, the fuel vapors enter a condenser, where they are condensed and flow into a receiver (a graduated cylinder). The temperature at which the first drop of fuel enters the receiver is recorded as the initial temperature of distillation.

Thereafter, in accordance with the specifications set forth for the fuel being tested, either the temperature at which a certain percentage of the fuel (10, 50, 90, 97, 97.5, 98%) has been collected in the graduated cylinder or the distilled percentages of the fuel that correspond to specified temperatures (100, 200, 260, 270°) are recorded.

If the terminal boiling temperature is normalized in the technical specifications for the fuel being tested, the flask is heated until the mercury column of the thermometer stops at a certain level and then begins to drop. The maximum temperature indicated in this process is recorded as the final temperature of the boiling range.

For fuels in which the temperature at which 97, 97.5 or 98% has boiled out is normalized, this temperature is taken as the end point for the fuel.

The small quantity of fuel that remains in the flask after distillation is measured and regarded as a residue. The difference between 100 ml and the sum of the residue and the distillate collected in the receiver is regarded as the distillation loss.

The fuel-quantity readings are taken to within 0.5 ml during distillation, while the temperature readings have an error of less than

The following discrepancies are tolerated for two parallel determinations of a fuel's fractional composition: 4° for the initial point of distillation, 2° and 1 ml for the end and intermediate points of fractional composition, and 0,2 ml for the residue. The results of distillation of a fuel may be presented in the form of a distillation curve (Fig. 9): the temperature is plotted against the axis of abscissas and the quantity of fuel (in percent) distilled at the temperature in question against the axis of ordinates.

The fractional composition of a fuel influences the performance of the engine and its service life. This influence is different for different engines: in some engines it is very strong and in others less noticeable.

Significance of fractional composition for a carburetor engine

The fractional composition of the fuel determines the manner in which the engine starts, the time required to warm it up, operating troubles due to vapor lock and carburetor icing, reliability, fuel consumption, the power developed by the engine, oil consumption and wear of rubbing parts, and particularly of the piston- and-connecting-rod assembly.

A relationship has been established between specific fractional-composition indices and the behavior of fuels in carburetor engines.

The temperature at which 10% of the fuel has boiled out is used as a basis for predicting its starting properties and its tendency to form vapor locks in the engine's fuel system. The lower the temperature at which 10% of the fuel has gone over, the better will be its starting properties and the more easily will the engine start on this fuel, but there will be a greater danger of vapor lock formation. The higher the temperature at which 10% of the fuel has gone over, the more difficult will it be to start the engine, but the lesser will be the danger of

vapor lock. In addition to the temperature of 10% distillation which has come into most extensive use as an index to the starting properties of a fuel, other points in the fractional composition which characterize the content of light fractions in the fuel may also be used to predict the starting properties of a fuel.

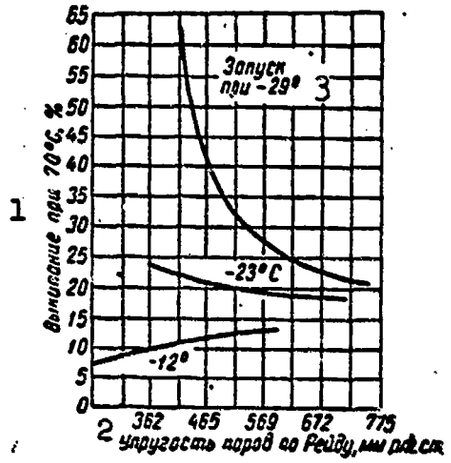



Fig. 10. Influence of distilled percentage of fuel and Reid vapor pressure on starting properties of gasoline. 1) Boiled out at 78% C, %; 2) Reid vapor pressure, mm Hg; 3) starting at -29°.

In combination with the Reid vapor-pressure indices, the percentage of the gasoline that has gone over at 70° gives a rather good characterization of the starting properties of a gasoline (Fig. 10). If the minimum starting temperature of an engine is -12° when a gasoline with a vaporizability of 10% at 70° is used, then a gasoline having the same vapor pressure but a vaporizability of 40% at 70° makes it possible to start the engine at a temperature as low as -29° [1].

The temperature at which 50% of the fuel has gone over characterizes its mean vaporizability, which influences the reliability, warmup time and operating stability of the engine. The lower the temperature at which 50% of the fuel has boiled out, the higher is its vaporizability and the better will be the reliability and operating stability of the engine on the grade of fuel in question.

The temperature at which 90% of the fuel has boiled out indicates that heavy fractions that are difficult to volatilize are present in the gasoline. The lower the temperature at which 90% of the fuel has gone over, the smaller is the amount of heavy fractions in it, the

TABLE 1

Operating economy on gasoline with vaporizability of 33% at 70° and 56% at 98.9° as compared with operation on gasoline with a vaporizability of 23% at 70° and 46% at 98.9° [1]

| Длина пробега, км 1 | 2Экономия бензина, %° | |
|---|---|---|
| | автомобиль А 3 | автомобиль Б 4 |
| 1,6 | 18,2 | 8,8 |
| 3,2 | 11,2 | 4,7 |
| 8,0 | 5,4 | 1,7 |
| 12,8 | 3,8 | 0,6 |

1) Distance travelled, km; 2) gasoline economy, percent; 3) vehicle A; 4) vehicle B.

complete will be the vaporization of the fuel in carburetion and the more uniform will be the distribution of the mixture among the cylinders.

The research of Academician Ye.A. Chudakov [2] and numerous operational tests have shown that heavy, hard-to-vaporize gasoline fractions have a highly detrimental influence on the performance of automobile engines. As the temperatures at which 50 and 90% of the fuel have boiled out rise, fuel consumption increases; the heavy fractions of the fuel are not burned. Some of them penetrate into the crankcase. Depending on the quantity of heavy fractions in the gasoline, the combustion efficiency may range from 10 to 70%.

Penetrating into the crankcase, the heavy gasoline fractions wash the oil from the cylinder walls and dilute the oil in the crankcase. This contributes to rapid wear of the engine parts and increased fuel consumption, since the diluted oil has a stronger tendency to enter the combustion chamber and pump out through defective seals in the crankcase.

The consumption of fuel in an engine depends not only on the presence of heavy, hard-to-vaporize fractions in the fuel, but also on the content of the fractions, which influence the reliability of the engine in wintertime operation.

After an engine has been started in winter, it should be allowed to run at low speed for a certain time in order to warm it up. The heavier the fuel, the more thoroughly must the engine be warmed up to

prevent flooding when the speed is increased. Consequently, when hard-to-vaporize fuels are used, the engine should be allowed to operate longer at a low throttle setting before being opened up than is the case when a readily vaporized fuel is employed. And the longer the warmup period at part throttle, the higher will be the consumption of gasoline.

When engines are operated under urban conditions, where stops are frequent and the distances travelled do not exceed a few kilometers, much fuel is consumed in warming them up. The influence of fuel fractional composition on fuel consumption involved in warming up the engine becomes more pronounced when the runs are shorter (see Table 1).

Influence of fuel fractional composition in the case of diesel fuel

In the case of a diesel engine, the fractional composition of a fuel influences fuel consumption, smoke content of exhaust, the ease with which the engine is started, carbon formation and nozzle coking, piston-ring scorching and wear of rubbing parts.

The sensitivity of the diesel-engine cycle to the fractional composition of the fuel depends in many ways on the manner in which the mixture is formed in the engine, since this influences the pressure, temperature and turbulence of the charge in the combustion process. The higher the pressure, temperature and turbulence of the charge, the less strongly will the influence of fuel fractional composition make itself felt in the combustion process.

High-speed diesels require a fuel with a lighter fractional composition than do low-speed diesels.

The use of a diesel fuel having a heavier-than-required fractional composition in high- and low-speed diesels increases fuel consumption, adversely affects starting, increases the rate of carbon-deposit formation, and causes coking of the nozzles, as well as a higher rate of

wear of the components and an increase in the exhaust smoke content.

An excessively light fuel fractional composition has an effect on diesel performance that is no less detrimental than that of excessively heavy fuels.

As the fractional composition of a fuel prepared from a given raw material becomes lighter, we have firstly a drop in cetane number; secondly, a drop in the viscosity of the fuel (at very low viscosity, wear of the fuel-supply apparatus increases, as does fuel leakage from the system); thirdly, we have an increase in the diesel's operating "hardness", since the quantity of mixture prepared for ignition depends on the speed with which the fuel is vaporized.

Saturation Vapor Pressure

The vapor pressure of a fuel, or the pressure of its saturated vapors, is one of the indices to its vaporizability.

Two standard methods are known for determining the saturation vapor pressures of fuels: the bomb method (after Reid, GOST 1756-52) and the Valyavskiy-Budarov method (GOST 6668-53).

GOST 1756-52 method

The vapor pressure is determined in an apparatus (Fig. 11) consisting of a steel bomb with two chambers: an upper air chamber with a capacity of 516 $cm^3$ and a lower gasoline chamber with a capacity of 129 $cm^3$, i.e., the capacity of the air chamber is to the capacity of the gasoline chamber as 4:1.

The chambers communicate through a tube. A manometer is inserted in the air chamber to measure the pressure. For a test, the lower chamber is filled with the fuel in question and the upper chamber screwed on over it with the manometer.

Assembled in this manner, the apparatus is immersed in a bath containing a liquid which is held at constant temperature.

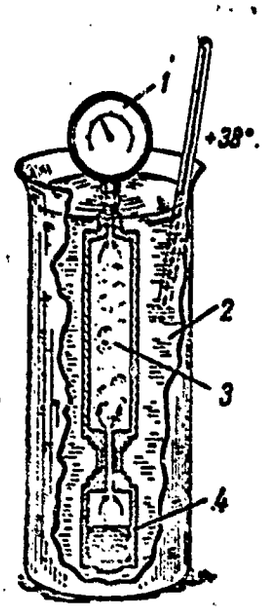



Fig. 11. Bomb for determining vapor pressure of gasoline. 1) Manometer; 2) water; 3) gasoline vapor; 4) gasoline to be tested.

After the apparatus has been immersed in the bath, the stopcock leading to the manometer is opened and the manometer is read after 5 min. Then the stopcock is closed, the apparatus is taken out of the bath, shaken vigorously, and replaced in the bath; the manometer reading is again noted.

These operations are repeated every 2 min. When the manometer reading no longer changes, the last reading is taken and corrected for the variation of air pressure as a function of temperature (computed by formula or taken from the tables) to obtain the fuel's saturation vapor pressure.

In accordance with the standard, the fuel vapor pressure is determined at 38.0° and measured in millimeters of mercury or in $kg/cm^2$. The vapor pressure of a fuel is influenced considerably by temperature and by the proportions between the vapor and liquid phases, so that the vapor pressure is determined at a certain constant vapor-to-liquid ratio and at constant temperature in order to obtain comparable figures.

The disagreement between parallel determinations may not exceed ±5 mm Hg from the arithmetic mean of the results being compared.

The Valyavskiy-Budarov method (GOST 6668-53)

The saturation vapor pressure of a fuel is determined from the increase in volume of the air- and-vapor mixture after the fuel has been evaporated in a gas burette at constant pressure and a 1:1 ratio between the initial volumes of the air and fuel.

The Valyavskiy-Budarov apparatus (Fig. 12) consists of the following basic parts: the burette 1 with the direct communicating stopcock

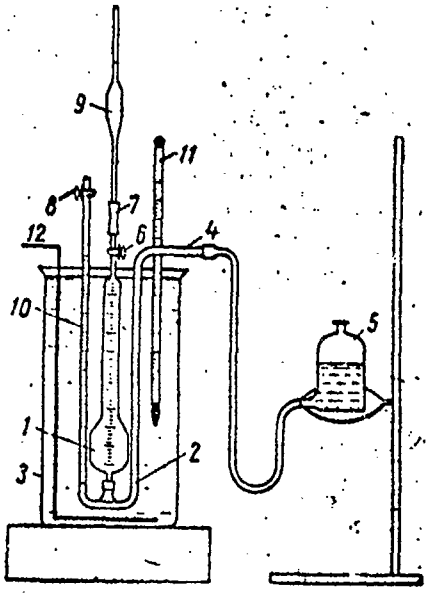



Fig. 12. Valyavskiy-Budarov apparatus.

the capacity of the burette being about 30 ml in the upper part and 20 to 25 ml in the lower part (it is graduated at 0.2-ml intervals at the top and 0.5-ml intervals at the bottom), the T-pipe 2, which is fitted with the siphon tube 4 and the barometric tube 10, the beaker 3 with the agitator 12, which serves as the bath, the thermometer 11 and the bottom-tube equalizing bottle 5. The bottle 5 is filled with a liquid that is not soluble in the fuel to be tested. For example, when hydrocarbon fuels are to be tested, water is normally used above 0° (with salt added), while antifreeze (a mixture of ethylene glycol with water) is used below 0°.

The following operations are performed to determine the saturation vapor pressure of the fuel. By raising the equalizing bottle 5 above the upper bend of the siphon tube 4 with the cocks 6 and 8 open, the burette is filled with liquid. Then the cock 6 is closed and the bottle 5 is lowered to a level at which the amount of air required for the test remains in the burette (the water is drained slowly from the burette and air admitted by cracking the cock 6).

Then, with the cock 6 closed, the bottle 5 is lowered to a level at which it is desired that the vapor- and-air mixture settle after expansion, and the fuel admitted cautiously into the burette from the pipette 9, which is connected by the section of rubber tube 7, through the cock 6.

After the equalizing bottle 5 has been adjusted so that the liquid level in the barometric tube 10 is at the same height as the fuel level in the burette and then held at this height for 5 minutes, the volume

of the vapor phase is read from the upper meniscus of the fuel in the burette.

The saturation vapor pressure of the fuel is computed by the formula

$$P_{\text{топ}} = \frac{V_2 V_1}{V_2} (P_{\text{ат}} - 49{,}7),$$

where $P_{top}$ is the saturation vapor pressure of the fuel in mm Hg, $V_1$ is the initial volume of the air (prior to evaporation of the fuel) in ml, $V_2$ is the volume of the air- and-vapor mixture (after evaporation of the fuel) in ml, $P_{at}$ is the atmospheric pressure in mm Hg and 49.7 is the saturation vapor pressure of the water in the burette at 38° in mm Hg.

The divergence allowed between parallel determinations is ±2% of the arithmetic mean of the results being compared.

The saturation vapor pressure is used as a basis for inferences as to the following:

1) the presence of readily vaporized fractions in the fuel that would contribute to the formation of vapor lock. The higher the fuel's saturation vapor pressure, the larger is its content of low-boiling fractions and, consequently, the greater is the danger of vapor-lock formation when an engine is operating on such a gasoline;

2) the starting properties of the fuel. The higher the saturation vapor pressure, the better the starting properties of the fuel and the shorter the time required to start and warm up the engine;

3) the possible losses of fuel due to evaporation during storage. The higher the saturation vapor pressure of the fuel, the greater will be the fuel losses.

High fuel vapor pressure results in formation of vapor locks and increased storage losses on the one hand and, on the other, it is a

determining factor for ease of starting and rapid warmup of the engine. It is impossible to reconcile such contradictory properties.

It is impossible to create a fuel that will not produce vapor locks and, at the same time, will insure easy starting of the engine in both winter and summer. Consequently, the fuels are produced with vapor pressures such that the tendency to vapor lock will be minimized while the fuel still possesses the required starting properties for summer and autumn. For starting the engine in winter, however, it is necessary either to preheat the engine or to use special starting fuels with high vapor pressures.

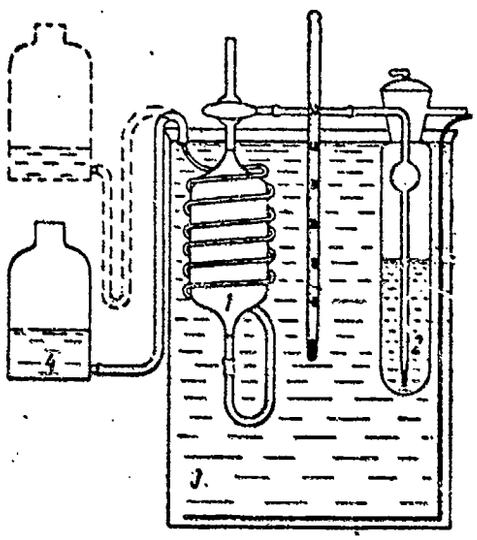


Fig. 13. Budarov apparatus.

Evaporation Losses

The Budarov method (GOST 6369-52) is used to evaluate the tendency of fuels to evaporation losses in decanting, fueling, storage, shipping and other handling operations.

The essence of the method consists in determining the weight loss of the fuel (in % by weight) after ten times the volume of air has been blown through it at 20° in a Budarov apparatus (Fig. 13). The apparatus consists of the following basic components: a measuring flask 1 with a capacity of 100 ml for measuring out the required quantity of air; the test tube 2, where the air is bubbled through the fuel, the beaker 3, which serves as the bath, and the equalizing bottle 4, the function of which is to displace the air from the measuring flask 1 with water flowing from the bottle into the measuring flask by the siphon effect.

Evaluation of the tendency of fuels to suffer evaporation losses,

using this method at 20°, give the following results (in % by weight).

| | |
|---|---|
| Isopentane | 15.6 |
| Automobile gasoline A-66 | 2.2 |
| Aviation gasoline B-100/130 | 1.4 |
| " " A-66 (direct-distilled) | 1.3 |
| " " B-95/115 | 1.0 |
| " " B-92 | 0.60 |
| Benzene | 0.41 |
| Ligroin | 0.14 |
| Rectified ethyl alcohol | 0.11 |
| Diesel fuel | 0.066 |

There is a relationship between evaporation losses and vapor pressure. The losses increase with a certain increasing rate as the vapor pressure rises.

VISCOSITY

Viscosity is the internal friction of a fluid.

Viscosity may be expressed in units of dynamic viscosity or in kinematic, specific, or arbitrary units.

If we take two layers, each with an area of 1 $cm^2$ in a fluid at a distance of 1 cm from one another and shift one layer relative to the other at a rate of 1 cm/sec, the resistance in dynes offered by the liquid will be its dynamic viscosity. The viscosity of a fluid that resists such displacement with a force of 1 dyne is taken as the unit dynamic viscosity.

The unit of dynamic viscosity expressed in the CGS system (centimeter-gram-second) is known as the poise. One-one hundredth of a poise is called a centipoise. The dimensions of the poise are dynes·sec/$cm^2$ or g/cm·sec.

The <u>kinematic viscosity</u> is the ratio of the dynamic viscosity to

the density of the liquid at the same temperature.

The unit of kinematic viscosity in the CGS system is the stoke. The dimensions of the stoke are $cm^2/sec$. One-one hundredth of a stoke is a centistoke.

The specific viscosity is the ratio of the dynamic viscosity of the fluid in question to the dynamic viscosity of water:

$$\eta_{уд} = \frac{\eta}{\eta_в}.$$

Normally, the dynamic viscosity of water at 20°, which is 1.005 centipoise, is used; consequently, the specific viscosity is higher by a factor of 100 than the dynamic viscosity, i.e.,

$$\eta_{уд} = \frac{\eta}{0{,}01} = \eta \cdot 100.$$

The arbitrary or relative viscosity is the viscosity expressed in arbitrary units as obtained on the various types of viscosimeters. Thus, the viscosity is measured in Engler degrees in the Engler viscosimeter, in Saybolt seconds in the Saybolt viscosimeter, and in Redwood seconds in the Redwood viscosimeter.

In the USSR, it is customary to express the arbitrary viscosity in VU degrees, which correspond to Engler degrees. Usually, the viscosities of fuels are determined in Ostwald-Pinkevich capillary viscosimeters (with three expansions) or in Volarovich viscosimeters (with four expansions) in accordance with GOST 33-53. The determination reduces to measurement of the time required for a certain volume of fuel to flow out through a capillary. By multiplying the time of fuel outflow by the capillary constant of the viscosimeter, we obtain the kinematic viscosity in centistokes; the viscosimeter constant is determined from the time of outflow of a standard liquid from the capillary in question at 20°. If it is necessary to express the viscosity of the fuel in VU degrees, the kinematic viscosity obtained is converted into VU degrees

by reference to formulas, tables, or graphs.

Viscosities are normalized in the GOST for ligroin, jet and diesel fuels, solar oil and mazouts.

The viscosities of ligroin and jet fuels are determined in the temperature range from +20 to -50°; those of diesel fuels are determined at +20 and +50°, those of solar oils at +50°, and those of mazouts at temperatures from 0 to 100°.

Viscosity is one of the most important quality indices of a fuel. It is a factor determining the fuel's evaporation and combustion properties, the operational dependability and longevity of the fuel [burning] apparatus and the possibility of using the fuel at low temperatures.

HEAT OF COMBUSTION

Heat of combustion is a term applied to the quantity of heat (in calories) liberated on complete combustion of 1 g or 1 kg of the fuel. This index was encountered earlier under the name "fuel heating value."

We distinguish between the upper-limit and lower-limit heats of combustion. The upper-limit heat of combustion is the quantity of heat liberated with condensation of the water vapor contained in the fuel prior to combustion and that formed during combustion. The lower-limit heat of formation is the quantity of heat liberated by 1 kg of fuel on complete combustion less the heat expended in evaporating the water present in the fuel before combustion and that formed in combustion.

The difference between the upper-limit and lower-limit heats of combustion ranges from 5 to 10% for petroleum products. Normally, the lower-limit heat of combustion is used for thermal-engineering calculations and to evaluate the heat of combustion of motor fuels.

The heat of combustion of a fuel, expressed in kilogram-calories per 1 kg of fuel (kcal/kg) is known as the unit-weight heat of combus-

tion, while that expressed in kilogram-calories per 1 liter of fuel (kcal/liter) is known as the unit-volume heat of combustion. The unit-volume heat of combustion is equal to the unit-weight heat of combustion multiplied by the density of the fuel.

The operating radius of an aircraft, motor vehicle or ship depends on the heat of combustion of its fuel, since the specific fuel consumption diminishes with increasing unit-weight heat of combustion and, for a given fuel-tank capacity, the fuel carried produces a greater heat effect as the unit-volume heat of combustion rises.

The heat of combustion is determined either by burning the fuel in calorimeters or by calculation from theoretical and empirical formulas. Two standard methods are known for determining the heats of combustion of petroleum products: the VTI method (GOST 5080-55) for determining the heats of combustion of liquid motor fuels and the bomb-combustion method (GOST 6712-53) for determining the heat of combustion of heavy petroleum products and petroleums that do not contain volatile products.

The VTI method (GOST 5080-55) consists in burning a weighed specimen of the fuel to be tested in a medium of compressed oxygen in a bomb calorimeter, measuring the quantity of heat liberated in this process, and computing the heat of combustion from the results of the experiment. A 0.5 – 0.6± 0.0002-g specimen of the fuel to be tested is placed in a Zubov dish.

The dish with the fuel is covered with a combustible film that is impermeable to the vapors of the fuel and then inserted in the bomb for combustion of the fuel. The heat of combustion is arrived at on the basis of the quantity of heat liberated during combustion of the weighed fuel specimen and expressed in calories per 1 g to within 10 cal.

The disagreement tolerated between two parallel determinations is

no greater than 30 cal/g.

The bomb method (GOST 6712-53) is similar to the VTI method, the only difference being that 0.6 – 0.8± 0.0002 g of the petroleum product to be tested is placed in a miniature crucible dish and not covered with the film. The heat of combustion is expressed in cal/g with an error of 10 cal. The disagreement between two parallel heat-of-combustion determinations may not exceed 30 cal/g.

STABILITY

Actual Tars

Actual tars are products that remain in the form of a solid or semiliquid residue in a glass beaker after fuel has been rapidly and completely evaporated from it. In other words, these are the tars present in the fuel in the dissolved state plus some that have formed during the experiment.

Actual tars occur for the most part in fuels that contain unsaturated hydrocarbons, which have a tendency to polymerize and form tars under the influence of oxygen, elevated temperature, and light. Such fuels include cracking gasolines and various mixtures of them.

The actual tars are determined in accordance with GOST 1567-56 or GOST 8489-58. The essentials of determining actual tars after GOST 1567-56 reduce to the following. Under a current of air, 25 ml of gasoline that has been heated to 150° (Fig. 14) is evaporated from a glass beaker. After evaporation of the gasoline, the beaker is weighed and the number of milligrams of tars per 100 ml of gasoline is determined.

Actual-tar contents below 2 mg per 100 ml of fuel are regarded as negligible amounts.

Budarov actual tars (GOST 8489-57) are determined by evaporating the fuel under a jet of steam in a special apparatus. The apparatus

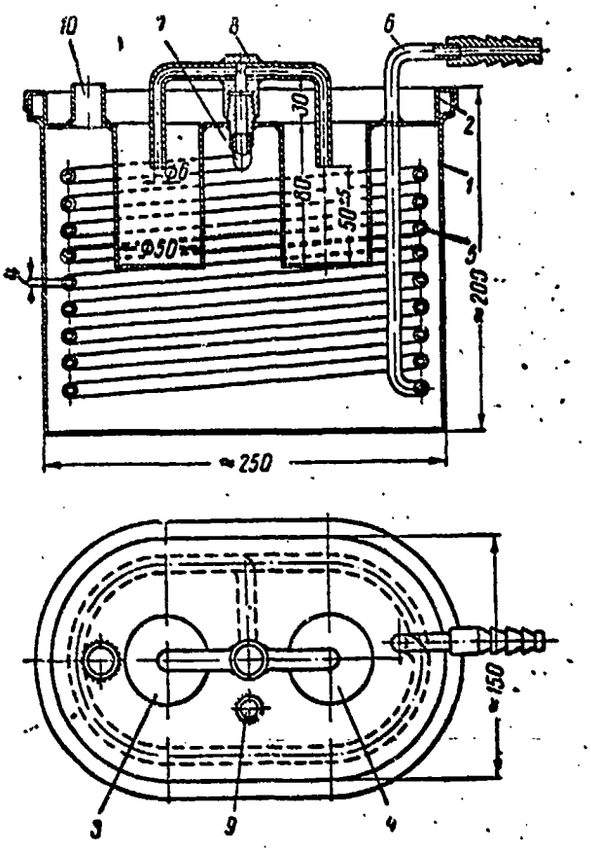



Fig. 14. Apparatus for determining actual tar content after GOST 1567-56. 1) Iron vessel; 2) removable iron cover; 3, 4) blind pockets for insertion of beakers; 5) copper coil; 6, 7) ends of coil; 8) removable ground T-pipe for delivery of air into beakers; 9, 10) holes for insertion of thermometer and temperature regulator.

consists of an oil bath in which two pockets for beakers with the fuel to be tested and two vessels whose function is to evaporate water (Fig. 15) are immersed. In determining the actual-tar content in gasolines, 25 ml of the gasoline to be tested are used and the experiment is run at 160±5°. In determining the actual tars in T-1, TS-1 and T-2 fuels, 20 ml of fuel are taken, while determinations in tractor kerosenes are made with 10 ml and the experiment is run at 185±5°. The results of the actual-tar determination are expressed in

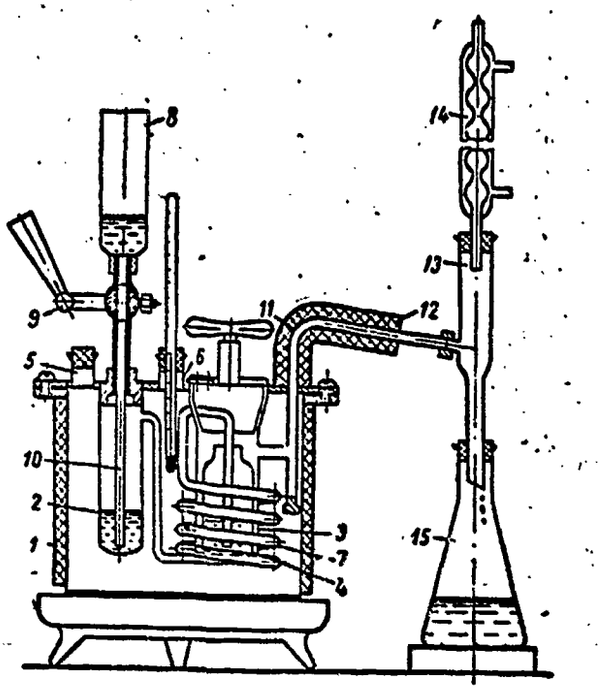



Fig. 15. Apparatus for determining actual tars after Budarov. 1) Cylindrical steel vessel with asbestos insulation; 2) vessel for evaporation of water; 3) blind pocket for insertion of beaker with fuel to be tested; 4) beaker; 5, 6) tubes for thermometers; 7) coil; 8) funnel; 9) stopcock; 10) tube for drainage of water into evaporator; 11) vapor offtake (steel tube to duct water and fuel vapor from pocket); 12) heat-insulation jacket on vapor offtake; serves to prevent condensation of vapor; 13) T-pipe for connecting vapor offtake with condenser and flask; 14) condenser; 15) flask.

mg/100 ml of fuel.

In aviation gasolines, the actual-tar content may not be greater than 2 mg per 100 ml of gasoline, while it may range from 2 to 20 mg in automobile gasolines, depending on grade.

As the quantity of tar in the gasoline increases, the rule is that octane number diminishes and the acidity of the gasoline in-

creases; the latter causes severe corrosion of the tanks. The color of the gasoline also changes when this happens: the gasoline becomes yellow and may even acquire a brown or black color.

An elevated content of actual tars in gasoline results in deposition of tars and carbon in the induction system, on the valves, and in the engine's combustion chamber.

Induction Period

Determination of actual tars enables us to form a judgment primarily as to the presence of tars in the gasoline. However, it is very important for the operational personnel to know how strongly the gasoline is inclined to tar formation and how long it can be stored.

The tendency of gasoline to form tars is evaluated by determination of the induction period (GOST 4039-48). 100 ml of gasoline are poured into a glass beaker, covered with a watch glass, and placed in a special metal bomb (Fig. 16). The bomb is filled with oxygen under a pressure of 7 atmospheres, lowered into boiling water, and held there until the manometer on the bomb indicates a pressure drop. This signals that the gasoline has begun to oxidize, i.e., that tars have begun to form in it.

The time (in minutes) during which the pressure in the bomb remained constant at a gasoline temperature of 100° is known as the induction period. If it is stated that the induction period of a gasoline is 240 minutes, this means that on heating in the bomb to 100° in the presence of oxygen, the gasoline began to oxidize after 240 minutes.

The longer the induction period, the more resistant the gasoline to tar formation, and the longer may it be stored without incurring the danger of tar formation.

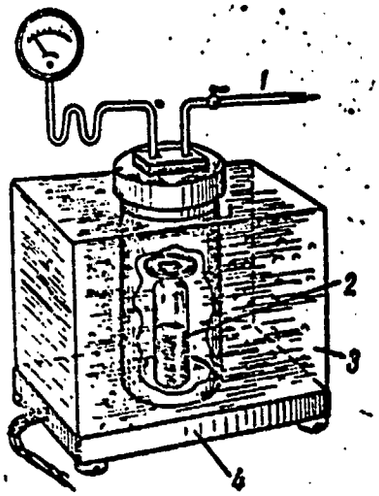



Fig. 16. Bomb for determination of of induction period of gasoline. 1) Oxygen; 2) gasoline; 3) water (100°); 4) electric oven.

Cokability of 10% residue

This index furnishes an arbitrary evaluation of the tendency of diesel fuels to form carbon deposits in engines. Fractional distillation is applied to 100 ml of the fuel to be tested and conducted in such a way that 10 ml of fuel remain in the flask after distillation. The determination is run in a standard apparatus at least 2 times in accordance with GOST 2177-59.

The cokability of the 10% diesel-fuel residue is determined in the apparatus used to determine the cokabilities of mineral oils (GOST 5061-49). A porcelain crucible receives a weighed specimen of about 8 g of the 10% residue. The crucible is then enclosed in two iron crucibles that are covered and placed under a bell and then heated. Having been heated to high temperature without access of air, the 10% residue vaporizes and decomposes, with the result that combustible gases are evolved and burn during the experiment, while the coke that has formed remains in the porcelain crucible. The coke content is expressed in percent of the weight of 10% residue poured into the crucible.

The cokability of the 10% residue from the diesel fuel to be tested is computed as the arithmetic mean of the results of two parallel determinations, between which a disagreement no greater than 20% of the smaller of the two results obtained is tolerated.

Method involving determination of maximum smokeless-flame height

Method involving determination of maximum smokeless-flame height is employed to evaluate the carbon-forming property of jet fuels:

this is familiar as the method used to evaluate the illuminating and heating ability of clear petroleum products when they are burned in lamps and heating devices. The essentials of the method are as follows. 10 ml of the fuel to be tested are poured into a specially designed lamp. After the lamp has burned for 5 minutes with a flame height of about 10 mm, the wick is raised so high that soot forms and then lowered until the soot has disappeared; then the height of the smokeless flame in mm is measured by reference to a height scale.

The greater the height of the smokeless flame, the higher is the quality of the product being tested.

Stability Period of Aviation Gasolines

When ethylated aviation gasolines are stored, lead compounds may precipitate in the form of solid deposits. Their stability during storage is evaluated by a method of determining precipitation resistance (GOST 667-56) developed by I.V. Rozhkov, G.S. Shimonayev and Ye.N. Kornilova. The essentials of the method are as follows. 25 ml of the gasoline to be tested are poured into a 100-ml glass bottle with a hermetically sealed stopper and heated to 100° in an LSA-1 apparatus (Fig. 17). Every half hour or hour a visual observation is taken to determine whether a precipitate has formed in the gasoline. The time at which a precipitate appears is fixed as the end of the test.

The time (in hours) for which no deposit forms in ethylated gasoline during oxidation by atmospheric oxygen at a temperature of 100° is taken as an index to the stability of the gasoline to formation of these sediments. The smaller time value obtained from parallel determinations in two bottles is taken as the test result.

A divergence of 1 hour is tolerated for stability periods less than 24 hours, and 2 hours for periods longer than 24 hours.

The stability period is used to judge the speed with which deposits may form in ethylated aviation gasolines as a result of decomposition of the ethyl fluid.

Ethylated gasolines having stability periods between 20 and 24 hours may be stored for 3 years at high temperature without danger of sediment formation in them. Ethylated gasolines with stability periods of 4 hours may be stored for approximately one year. On the other hand, it is recommended that gasolines with stability periods less than 4 hours be used at the first opportunity, since the possibility that sediment may appear in such a gasoline in a few months of storage cannot be excluded.

THERMAL STABILITY

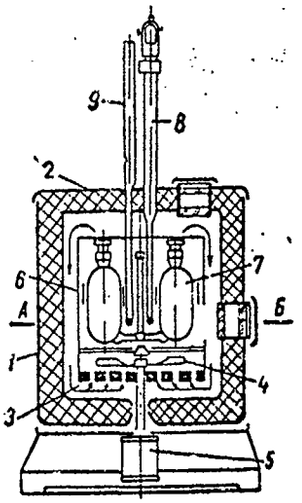
Thermal stability characterizes the resistance of a fuel to formation of sediments on heating in the presence of air. Thermal stability is determined by the method developed by I.V. Rozhkov (GOST 9144-59). The essentials of the method consist in oxidation of 50 ml of the fuel in an LSA-1 apparatus (see Fig. 17) at a temperature of 150° for 1 hour. The fuel that has been oxidized is filtered through an ash-free paper filter and the quantity of sediment that has formed is determined by weighing. The thermal stability is expressed in milligrams of sediment per 100 ml of fuel.

CORROSION PROPERTIES

Copper-Plate Test

The copper-plate test (GOST 6321,52) serves for detection of active sulfur compounds and free sulfur, which cause corrosion of metals, in the fuel.

A standard-size copper plate made from pure electrolytic copper is held in the fuel for 3 hours at 50°, and its surface is then compared with a bright plate that has not been subjected to this test.

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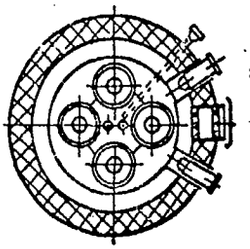

Fig. 17. LSA-1 apparatus for determining thermal stability of fuels. 1) Cylindrical housing; 2) cover; 3) open-type electric heater grid; 4) fan; 5) electric motor; 6) diffuser; 7) cartridges with four flasks; 8) handle for turning cartridges with flasks; 9) inspection window; 10) electric light bulbs; 11) contact thermometer; 12) monitoring mercury thermometer. a) Section through AB.

The appearance of black, dark-brown or steel-gray deposits and stains on the plate indicates that active sulfur compounds capable of causing corrosion in an engine or in a fuel system are present in the fuel. If any other changes or no color changes at all have occurred on the plate, the fuel is considered to have passed the test.

Sulfur

In light petroleum products (gasoline, kerosene, diesel fuel), sulfur is determined in accordance with GOST 1771-48 by burning a weighed specimen of the test fuel in a lamp (Fig. 18). The sulfur trioxide formed during combustion is trapped and the quantity determined volumetrically. From 1.5 to 5 ml of fuel is required for the experiment, depending on the sulfur content in it.

A divergence no greater than 5% of the smaller result is tolerated between two parallel determinations.

The sulfur content in aviation and automobile gasolines and that in jet and diesel fuels is strictly limited by the corresponding GOST standards. This is the result of the following causes: 1) sulfur and sulfur compounds have a corrosive effect on the engine and contribute to formation of deposits; 2) a high sulfur content lowers the antiknock properties of the gasoline – octane number and grade; 3) certain sulfur compounds

sharply reduce the sensitivity of the gasoline to tetraethyl lead.

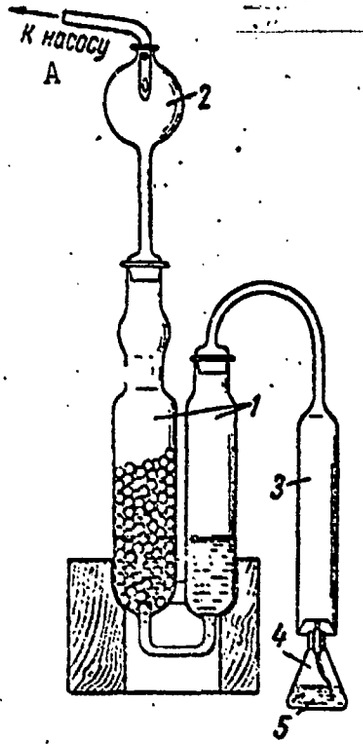


Fig. 18. Apparatus for determining sulfur by lamp method. 1) Adsorber; 2) spatter trap; 3) lamp chimney; 4) lamp; 5) wick. A) To pump.

Mercaptan sulfur

The mercaptan-sulfur content in a fuel is determined in accordance with GOST 6975-57. The essentials of the method consist in titrating the fuel to be tested with an ammonia solution of copper sulfate. The mercaptans of the fuel react with the ammonia solution of copper sulfate to form copper mercaptides. The disagreement between two parallel determinations may not exceed 0.0005% on the amount of fuel. Mercaptan sulfur causes severe corrosion of metals, so that a content no greater than 0.01% is permitted in T-2 and TS-1 fuels.

Hydrogen Sulfide

Freedom of diesel and jet fuels from hydrogen sulfide is checked by the following method. 10 ml of a 2% solution of caustic soda are added to 10 ml of the fuel in a separating funnel, thoroughly shaken, and, after standing, 3 to 5 ml of the extract are placed in a test tube, acidified with 0.4 to 0.6 ml of concentrated hydrochloric acid and heated with shaking to 70 — 80°. In the presence of hydrogen sulfide, lead indicator paper touched to the rim of the test tube changes color from light brown to dark brown.

Diesel fuel with a hydrogen sulfide content is not suitable for use because of its high corrosion properties and its strong tendency to form varnish deposits and carbon.

Organic Acidity

The acidity of fuel is determined in accordance with GOST 6041-51; the organic acids are extracted from the fuel with boiling ethanol and titrated with a solution of potassium hydroxide. The acidity is expressed in terms of mg of KOH required to neutralize 100 ml of fuel.

The acidity of the fuel serves as a basis for inferences as to its content of acidic compounds. Such compounds include naphthenic acids, phenols, asphaltogenic acids, and the like. The naphthenic acids, particularly the low-molecular-weight members are capable of causing corrosion of tanks and the parts of the engine's fuel-supply system. Most severely attacked by naphthenic acids are lead, copper, tin, steel and iron; naphthenic acids do not attack aluminum. Soaps form when naphthenic acids react with metals; usually, these soaps are insoluble in the fuel and remain suspended in it, although they may settle out in the form of a precipitate.

The presence of soaps in the fuel represents an extremely serious danger, since they may clog the filters and nozzles of the fuel system and cause cutoff of the fuel supply to the engine.

LOW-TEMPERATURE PROPERTIES

The low-temperature properties of a fuel are judged from its cloud point, initial crystallization temperature, and pour point.

The cloud point and initial crystallization temperature are determined in accordance with GOST 5066-56.

The cloud point of a motor fuel is the temperature at which the fuel begins to show turbidity as a result of separation of microscopic water droplets or ice or hydrocarbon microcrystals.

The initial crystallization temperature of a motor fuel is the maximum temperature at which ice or benzene crystals can be detected in the fuel with the unaided eye. The essentials of cloud-point and

crystallization-point determination consist in the following (Fig. 19).

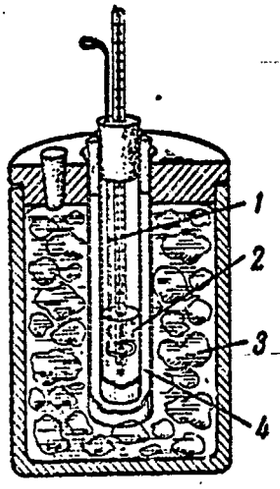


Fig. 19. Apparatus for determining freezing point and cloud point of gasoline. 1) Agitator; 2) gasoline to be tested; 3) dry ice in alcohol; 4) air.

A standard glass test tube with an agitator is placed in another test tube which serves as an air bath, and the entire arrangement is placed in an insulated cylindrical vessel with a coolant mixture (alcohol and dry ice). The fuel poured into the test tube equipped with the agitator is cooled and observed either for clouding or for the appearance of crystals, depending on which property is to be determined.

The pour point is determined in accordance with GOST 1533-42. A standard test tube with the fuel is placed vertically in the coolant mixture, held there for 5 minutes, and then tilted at a 45° angle and left in this position for 1 more minute at the same temperature.

The pour point of the fuel is the temperature at which the fuel becomes so thick under the experimental conditions that the level remains stationary for 1 minute when the test tube is inclined at a 45° angle.

For gasolines and jet fuels, the cloud and initial-crystallization temperatures are checked; for diesel fuels, the cloud point and pour point are checked.

CONTROL INDICES

Density

Density is customarily denoted by the symbol $\rho_4^{20}$. The superscript indicates the temperature of the product, and the subscript the temperature of the water. Density may be measured with an aero-

meter (petroleum densimeter), a Westphal balance or a pycnometer.

In some countries, a Baume (Be) or API-scale aerometer is used to determine density.

The following formulas are used for the conversion:

$$\rho_4^{20} = \frac{141{,}5}{131{,}5 + {}^\circ\text{API}}$$

and

$$\rho_4^{20} = \frac{140}{130 + {}^\circ\text{Bé}}.$$

The densities expressed in Baume or API degrees are extremely close together.

Density increases as the temperature drops and diminishes as it rises. Consequently, in order to obtain comparable figures it is customary to reduce the temperature to 20°, regardless of the temperature at which it was measured. Correction factors are available for this purpose.

Density is computed according to the formula

$$\rho_4^{20} = \rho_4^{t} + \gamma (t - 20),$$

where $\rho_4^{20}$ is the density of the product at 20°, $\rho_4^{t}$ is the density of the product measured at the temperature in question, $\gamma$ is a density correction and $t$ is the temperature of the product at the time of the density determination.

Iodine Number

The iodine number is the quantity of iodine in grams that combines with 100 g of fuel. The iodine number indicates the relative content of unsaturated compounds in the fuel.

Determination of n-hydroxydiphenylamine

The content of the antioxidant n-hydroxydiphenylamine in aviation gasolines is determined by the method of GOST 7423-55, which was developed by I.V. Rozhkov. The essence of the method consists in extracting

the n-hydroxydiphenylamine from the fuel with a solution of hydrochloric acid and then determining its content in the extract by addition of hydrogen peroxide. The divergence tolerated between parallel determinations may not exceed ±10% of the arithmetic mean of the results being compared.

Ash Content

The ash content of a fuel is determined by the method of GOST 1461-52. 25 g of fuel is evaporated in a crucible. The residue is heated to a dark red glow until it is fully converted to ash. The ash thus obtained is expressed as a percentage of the weighed sample of fuel taken.

The discrepancy between two parallel ash-content determinations on the fuel to be tested may not exceed the following values.

| Ash Content, % | Permissible Divergence, % |
|---|---|
| Below 0.005 | 0.002 |
| From 0.005 to 0.01 | 0.003 |
| From 0.01 to 0.1 | 0.005 |
| Above 0.1 | 0.01 |

Mechanical Impurities

Mechanical impurities in fuel are determined by the gravimetric method of GOST 6370-52.

100 g of fuel are filtered through an ash-free filter, which traps the mechanical impurities; then the filter is dried and weighed. The mechanical impurities obtained are expressed as a percentage of the weighed fuel specimen taken. A fuel containing less than 0.005% of mechanical impurities is regarded as free of them.

The following discrepancies are tolerated between parallel determinations.

| Mechanical-impurity content, % | Permissible Disagreement, % |
|---|---|
| Below 0.01 | 0.005 |
| 0.01 – 0.1 | 0.01 |
| >0.1 | 0.02 |

Mechanical impurities in fuels are normally detrimental to jet engines and high-speed diesels, since the fuel pumps and nozzles of these engines are fabricated to high precision specifications and are very sensitive even to extremely fine impurity particles.

While mechanical impurities settle to the bottom of the tank quite rapidly by gravity when present in a gasoline, the same particles will remain much longer in the suspended state in the case of diesel and jet fuels. Foreign impurities in a fuel may be the cause of rapid and severe wear of the fuel-supply apparatus and even put it out of commission.

Determination of Water Content

The hygroscopic-water content in aviation and other motor fuels is determined by the method of GOST 8287-57. The method is based on the reaction of calcium hydride with the water present in the fuel and measurement of the volume of hydrogen liberated in this reaction. A diagram of the apparatus is shown in Fig. 20. The water content in the fuel tc be tested is computed in percent by weight.

Water-Soluble Acids and Alkalis

Fuels must be free of alkalis and mineral acids, since they cause severe corrosion of metals. The presence of these substances is established by the reaction of a water extract.

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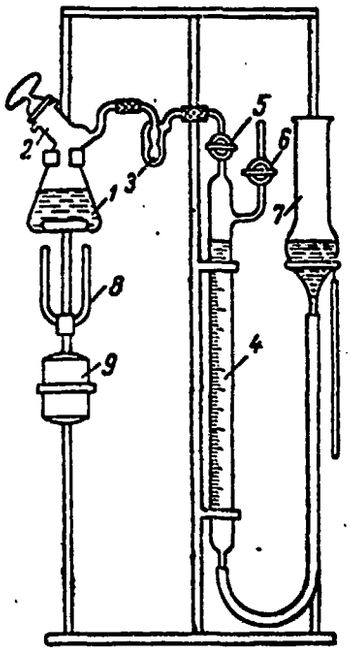


Fig. 20. Apparatus for quantitative determination of water content in motor fuels. 1) Conical flask; 2) stopcock stopper; 3) Drechsel bottle; 4) gas burette; 5) stopcock connecting burette with Drechsel bottle; 6) stopcock connecting burette with atmosphere; 7) leveling bottle; 8) horseshoe magnet; 9) electric motor.

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| Manuscript Page No. | [List of Transliterated Symbols] |
|---|---|
| 48 | топ = top = toplivo = fuel |
| 48 | ат = at = atmosfernyy = atmospheric |
| 51 | уд = ud = udel'nyy = specific |
| 51 | в = v = voda = water |

## Chapter 4

## EVALUATION OF KNOCK-RATING STABILITY AND IGNITION QUALITY OF FUELS

### GENERAL DATA

Among the indicators characterizing the motor properties of gasolines and tractor kerosenes, the knock-rating stability (antiknock properties) is one of the most important. It is for this reason that the technical specifications for these types of fuels impose rigorous controls on the antiknock values.

Researchers first encountered knocking in engines in 1919.

The first methods employed to determine the antiknock properties of fuels (1920-1927) were based on the utilization of specially equipped engines. The magnitude of the antiknock value was expressed in the unit of the critical compression ratio (the highest effective compression ratio, NPSS) or in the units of fuel equivalents – aniline, benzene, or toluene.

All of these methods fail to provide good reproducibility of results and those obtained were in poor agreement with the characteristics of these engines under operating conditions. It was for this reason that these methods were employed on a restricted basis only.

The generally recognized indicator of the antiknock property of a fuel is the octane number. This indicator was adopted in 1927 when two individual hydrocarbons – isooctane (2,2, 4 trimethylpentane, $C_8H_{18}$) and n-heptane ($n\text{-}C_7H_{16}$) exhibiting markedly different anti-

TABLE 2

Knock-rating Stability of Individual Hydrocarbons Expressed in Various Units

| 1 Углеводород | 2 Критическая степень сжатия | 3 Анилиновый эквивалент | 4 Октановое число (моторный метод) |
|---|---|---|---|
| 5 Бензол | 15,0 | +10 | > 100 |
| 6 Изооктан | 7,7 | +16 | 100 |
| 7 Изопентан | 5,7 | + 9 | 90 |
| 8 Метилциклопентан | 4,6 | + 4 | 82 |
| 9 н-пентан | 3,8 | + 1 | 64 |
| 10 н-гексан | 3,3 | — 6 | 59 |
| 11 н-гептан | 2,6 | —14 | 0 |

1) Hydrocarbon; 2) critical compression ratio; 3) aniline equivalent; 4) octane number (motor method); 5) benzene; 6) isooctane; 7) isopentane; 8) methylcyclopentane; 9) n-pentane; 10) n-hexane; 11) n-heptane

knock properties – were proposed as standard fuels for the evaluation of the antiknock properties of fuels. Isooctane has a high antiknock value, whereas n-heptane has an extremely low antiknock value. For example, on an experimental engine with a variable compression ratio, when operating on isooctane, engine knocking appears with a compression ratio of 7.7, whereas with n-heptane the knocking begins with a compression ratio of 2.8.

The antiknock property in the case of isooctane has been set at 100 units, by convention, and this property for the case of n-heptane has been set at zero. By preparing a mixture of isooctane with n-heptane (in %, by volume), it becomes possible to prepare standards exhibiting antiknock values ranging from zero to 100 units. The isooctane percentage in the mixture with n-heptane is referred to as the octane number. Essentially, the determination of the octane numbers involves the testing of a gasoline with an unknown antiknock value and standards, i.e., mixtures of isooctane with n-heptane, in a special single-cylinder engine; by the continuous switching of the engine to operate

on the specimen being tested and the standard, it becomes possible to select such a standard mixture as exhibits an antiknock value that is identical to the gasoline specimen being tested. Consequently, the octane number of gasoline characterizes its antiknock value and is numerically equal to the percentage content of isooctane in this standard mixture (with n-heptane), which under standard test conditions on the special engine exhibits an antiknock value that is the same as that of the gasoline being tested. For example, the gasoline being tested has an antiknock value like that of a mixture of 90% isooctane + 10% n-heptane; this means that the gasoline has an octane number of 90.

Table 2 presents data on the antiknock values of individual hydrocarbons.

There are a number of methods for the determination of fuel octane numbers. Because of the differences existing in the testing conditions, the obtained octane-number values for various fuels may exhibit substantial divergence. For example, gasoline may have an octane number of 70 according to one method, whereas its octane number may be 78 with another method, etc.

For this reason it is extremely important, in addition to the octane number, to know the method which was employed to determine this octane number. Of all the methods used to determine the octane numbers of fuels, the following are the most commonly used: the motor method, the research method, and the temperature methods [aviation (lean mixture) and supercharge (rich mixture)] (Table 3).

The motor method of determining octane numbers was developed in 1932 in connection with the fact that results from the determination

of octane numbers by the research method that was in use at that time were not in sufficient agreement with the behavior of fuels in automotive engines. Moreover, because of the imperfections of the equipment being used to measure antiknock properties, the results exhibited poor capacity for reproduction in parallel determinations (the deviations between the parallel determinations frequently attained 8-10 octane units).

On the basis of results obtained in a wide range of investigations, a number of improvements were introduced into the research-method installation: the design of the equipment employed for the measurement of the antiknock value was improved, the carburetor was replaced, and the conditions under which the tests were being carried out were also altered, i.e., the rpm of the engine was increased to 900 rpm (instead of 600 rpm); another innovation was the introduction of the procedure to heat the working mixture to 150°, and to heat the crankcase oil to 55-65°. Numerous tests of various gasolines according to the motor method showed that this method provides the best reproducibility of results in parallel determinations and from various installations, and these results exhibit the best agreement with the behavior of fuels in actual automotive engines.

The motor method is the most commonly used method of evaluating antiknock properties and is widely used at the present time for the determination of the octane numbers of gasolines and kerosenes.

The research method of determining octane numbers for automotive gasolines was adopted in 1939. The need for this method came about as a result of the fact that the motor method was not always able to provide a reliable evaluation of the antiknock property of automotive gasolines whose composition was subject to substantial change.

The new method was based on the old research method that had been

in use prior to 1932, but certain changes were introduced: the same equipment as was used in the motor method was employed here to measure the antiknock value; a permanent ignition-lag angle was established (13° before top (dead) center) for all compression ratios; in addition, a suction valve with a special screen to mix the working mixture was installed (this device was the same as that employed in the motor-method engine); and finally, the intake air was heated to 52°. The remaining conditions correspond to the old research method of determining octane numbers.

Laboratory and particularly extensive road tests, carried out in 1946, 1949, 1951, and 1954, have demonstrated that the research method of determining the octane numbers is better than the motor method in characterizing the antiknock property of automotive gasolines for actual operating conditions such as city driving (frequent stops and, as a rule, reduced power with less thermal stress on the engine).

Country driving, particularly on long trips, makes possible engine operation that is characterized by a constant operating regime and, consequently, by great thermal stress. For these conditions, a more valid evaluation of antiknock properties is offered by the motor method.

The results obtained in an evaluation of antiknock values according to the research method are in better agreement with the road ratings (the road method of determining octane numbers for fuels in automotive engines).

As of 1948, the research method (1939) is in wide use abroad, together with the motor method, for the determination of the octane numbers of automotive gasolines.

The temperature method of determining the antiknock values for aviation gasolines was developed in 1942 in connection with the ex-

panding production of high-octane aviation gasolines and components.

The motor and research methods for the determination of octane numbers make it possible to carry out a sufficiently accurate evaluation of fuels having octane numbers below 95 units. Fuels with higher antiknock values are difficult to evaluate with the above-mentioned methods because of the unreliable operation of the apparatus employed to measure the knocking (the electromechanical sensing element) (sensor) for knocking), in the case of high compression ratios, and consequently, in the case of high pressures in the combustion chamber.

However, the need for such an evaluation existed with respect to aviation gasolines (100/130, 115/145) and particularly with respect to the numerous high-octane components.

All of this made it an absolute must that a new method be developed for the evaluation of the antiknock properties of fuels, and this method was designated as the temperature method which is intended for high-octane aviation gasolines.

The test installation for this method is basically the same single-cylinder installation as was used in the motor method, but certain structural changes have been introduced.

To match the fuel-testing conditions of this method to operating conditions of aviation engines, a more rigid operating regime than had been employed with the motor method was established for the single-cylinder engine: the temperature of the cooling liquid (coolant) is 190° and the oil temperature is 75°; a constant 35° crank-angle lag before top (dead) center was established for all compression ratios, etc., and the rpm of the engine was increased to 1200 rpm).

The basic difference between the temperature method and the motor and research methods can be found in the manner in which knocking is measured, the latter based on the measurement of the average tempera-

tures of the combustion-chamber walls by means of thermocouples and a potentiometer in the case of detonating combustion of the fuel. (This method was taken from the U.S. Army method for the determination of octane numbers.)

This method provided for the reliable determination of antiknock properties of aviation gasolines with octane numbers ranging from 90 to 115.

In recent years, with conversion to turbojet and turboprop engines and in view of the significant reduction in the role of aviation gasolines, the use of the temperature method has been greatly restricted. This method is used only at petroleum refineries producing high-octane aviation gasolines.

Fuel Sensitivity

Investigations and tests have demonstrated that automotive gasolines exhibit various antiknock values, depending on the composite chemical composition at various engine-operating regimes. This behavior of automotive gasolines is associated with their various sensitivities to engine-operating regimes.

An explicit example of this property on the part of automotive gasolines is the difference between the octane numbers determined by the motor and research methods, said difference attributable to the differences between the test regimes (Table 3).

In this connection, for a more complete characteristic of the operational properties of automotive gasolines an additional indicator of antiknock value has been introduced, and this indicator is referred to as fuel "sensitivity."

The sensitivity of automotive gasolines is expressed by the difference in octane numbers determined on the basis of the research and motor methods.

TABLE 3

Methods for the Determination of Antiknock Properties of Fuels

| 1 Основные параметры, характеризующие условия проведения испытаний | 2 Моторный метод ГОСТ 511-61 | 3 Исследовательский метод ГОСТ 8226-61 | 4 Авиационный с наддувом ГОСТ 3338-61 | 5 Температурный метод ГОСТ 3337-52 |
|---|---|---|---|---|
| 6 Число оборотов двигателя в минуту | 900 | 600 | 1800 | 1200 |
| 7 Температура охлаждающей жидкости, °С | 100,0 | 100,0 | 100,5 | 100.5 |
| 8 Температура всасываемого воздуха, °С | 25—50 | 25 25—50 | 107 | 52 |
| 9 Температура рабочей смеси, °С | 150,0 | Не контролируется | Не контролируется | 105,0 |
| 10 Температура масла в картере, °С | 19 50—65 | 26 То же | 28 75—80 | 50—70 |
| 11 Угол опережения зажигания, град. | 26° до в. м. т. при степени сжатия 5,0. | 27 13° до в. м. т. для всех степеней сжатия | 45° до в. м. т. при степени сжатия 7,0 | 35° до в. м. т. для всех степеней сжатия |
| | 20 Переменный | | 29 Постоянный | Постоянный |
| 12 Способ измерения детонации | 21 Электромеханический датчик детонации | | 30 На слух или детонометром | 34 Термопара |
| 13 Способ изменения интенсивности детонации | 22 Изменением степени сжатия | | 31 Изменением наддува | 35 Изменением степени сжатия |
| 14 Единицы оценки детонационной стойкости | 23 Октановое число | | 32 Сортность или индексовое число | 36 Октановое число или условная сортность |
| 15 Соответствие результатов оценки составу рабочей смеси | 24 Бедным смесям ($\alpha = 0{,}95 \div 1{,}05$) | Бедным смесям ($\alpha = 0{,}9$) | 33 Богатым смесям ($\alpha = 0{,}8 \div 0{,}85$) | Бедным смесям ($\alpha = 0{,}85 \div 0{,}95$) |
| 16 Диаметр цилиндра двигателя, мм | 85,0 | 85,0 | 85,0 | 85,0 |
| 17 Ход поршня, мм | 115,0 | 115,0 | 115,0 | 115,0 |
| 18 Рабочий объем цилиндра, л | 0,652 | 0,652 | 0,652 | 0,652 |

1) Basic parameters characterizing test conditions; 2) motor method, GOST [All-Union State Standards] 511-61; 3) research method, GOST 8226-61; 4) aviation method with pressure feed, GOST 3338-61; 5) temperature method, GOST 3337-52; 6) engine rpm; 7) coolant temperature, °C; 8) temperature of intake air °C; 9) temperature of working mixture, °C; 10) temperature of crankcase oil, °C; 11) crank-angle ignition lag, deg; 12) method of measuring antiknock value; 13) method for changing knocking intensities; 14) ratings (units) for evaluation of antiknock values; 15) agreement of evaluation results to composition of working mixture; 16) diameter of engine cylinder, mm; 17) piston stroke, mm; 18) cylinder capacity, in liters; 19) 26° before top center at a compression ratio of 5.0; 20) variables; 21) electromechanical sensing element for knocking; 22) with change in compression ratio; 23) octane number; 24) lean mixtures; 25) not checked; 26) the same; 27) 13° before top center for all compression ratios; 28) 45° before top center at a compression ratio of 7.0; 29) constant; 30) by ear or by means of a detonometer; 31) by changing the pressure feed; 32) grade or index number; 33) rich mixtures; 34) thermocouple; 35) by a change in the compression ratio; 36) octane number or conventional grade.

To evaluate the sensitivity of automotive gasoline, we must determine the octane numbers according to both the research and motor methods, and then from the octane number determined from the research method, to subtract the octane number derived on the basis of the motor method.

The sensitivity of hydrocarbons is not identical and is a function of their chemical composition and structure (Table 4).

The olefinic hydrocarbons are the most sensitive, the aromatic hydrocarbons being only slightly less sensitive. Paraffinic hydrocarbons exhibit very low sensitivity. Naphthenic hydrocarbons occupy an intermediate position; according to this indicator, the latter lie between the paraffinic and aromatic hydrocarbons.

Rich-Mixture Fuel Grades

The antiknock property of fuels is determined on the basis of the motor, research, and temperature methods for a working-mixture composition corresponding to maximum knock, i.e., for an excess-air ratio of $\alpha = 0.85\text{-}1.1$, and this corresponds to lean mixtures. Therefore the results obtained by means of these methods serve as the antiknock characteristics of lean mixtures.

Aviation piston engines operate primarily in two regimes: at maximum power for take-offs, and at cruising speeds.

In the case of take-off regimes, the engines operate on rich mixtures ($\alpha = 0.7\text{-}0.8$); in the cruising-speed regime the engines operate on lean mixtures ($\alpha > 1.0$).

In thrust-augmented operation of aviation piston engines, cases have frequently been observed in which gasolines with identical octane numbers behaved differently with respect to one another under the conditions of their utilization in these engines, i.e., one gasoline would provide for knock-free engine operation in all regimes, whereas

TABLE 4

Hydrocarbon Sensitivity (after Gerp [sic] and Smit [sic])

| 1 Углеводороды | 2 Октановое число | | 5 Чувствительность (им — мм) |
|---|---|---|---|
| | 3 исследовательский метод (им) | 4 моторный метод (мм) | |
| 6 *Парафиновые* | | | |
| 7 Изобутан | 101,1 | 97,6 | +4,5 |
| 8 Изопентан | 92,3 | 90,3 | +2,0 |
| 9 Изогексан | 91,8 | 93,4 | —1,6 |
| 10 Изооктан | 100,0 | 100,0 | 0,0 |
| 11 н-Бутан | 93,6 | 90,1 | +3,5 |
| 12 н-Пентан | 61,7 | 61,9 | —0,2 |
| 13 н-Гексан | 24,8 | 26,0 | —1,2 |
| 14 *Олефины* | | | |
| 15 Пропилен | 101,4 | 84,9 | +26,3 |
| 16 Изобутилен | 101,5 | 88,1 | +23,4 |
| 17 Пентен-1 | 90,9 | 77,1 | +13,8 |
| 18 Гексен-1 | 76,4 | 63,4 | +13,0 |
| 19 *Нафтены* | | | |
| 20 Метилциклопентан | 91,3 | 80,0 | +11,3 |
| 21 Этилциклопентан | 67,2 | 61,2 | + 6,0 |
| 22 Изобутилциклопентан | 33,4 | 28,2 | + 5,2 |
| 23 Метилциклогексен | 46,5 | 40,8 | + 5,7 |
| 24 *Ароматические* | | | |
| 25 Бензол | >100,0 | 108,0 | — |
| 26 Толуол | 115,0 | 103 | +12 |
| 27 Этилбензол | 106,0 | 97,9 | + 8,1 |
| 28 Изопропилбензол (кумол) | 110,0 | 99,3 | +10,7 |

1) Hydrocarbons; 2) octane number; 3) research method (rm) ; 4) motor method (mm); 5) sensitivity (rm - mm) ; 6) paraffinic; 7) isobutane; 8) isopentane; 9) isohexane; 10) isooctane; 11) n-butane; 12) n-pentane; 13) n-hexane; 14) olefinic; 15) propylene; 16) isobutylene; 17) pentene-1; 18) hexene-1; 19) naphthenic; 20) methylcyclopentane; 21) ethylcyclopentane; 22) isobutylcyclopentane; 23) methylcyclohexene; 24) aromatic; 25) benzene; 26) toluene; 27) ethyl benzene; 28) isopropylbenzene (cumene).

the other would exhibit knocking during the take-off regime.

It was subsequently determined that gasolines exhibit various antiknock properties (depending on their chemical composition) not only in the case of lean mixtures but in the case of rich mixtures as well and it was further established that a single octane number is not adequate fully to characterize the antiknock properties of a gasoline.

In connection with the divergent behavior of fuels in the case of lean and rich mixtures under pressure-feed conditions, a new method was developed in 1942 for the evaluation of the antiknock properties of rich-mixture aviation gasolines, and this method was designated as the method for the determination of grades of rich-mixture aviation gasolines. Essentially, the determination of grade involves the comparison of the fuel specimen being tested with the reference fuels whose grades are known. The determination is carried out on a special single cylinder engine operating under rigorously maintained constant conditions. The basic indicator in this comparison is the magnitude of the maximum value of the mean indicator pressure $p_i$ which is developed in the cylinder of an engine operating in an initial detonation regime. For the specimen being tested we select a reference fuel which will exhibit the same mean indicator pressure as the specimen for initial detonation.

As the reference fuels in grade determination we use isooctane in its pure form as well as various quantities of tetraethyllead (TES = TEL), added in the form of an ethyl fluid.

The grading (performance numbers) for the reference fuels was established experimentally by the testing of these reference fuels in single-cylinder installations which had been equipped with the various cylinders employed in mass-produced aviation engines. During these tests each reference fuel was made to detonate (knock) by increasing the pressure feed to the engine, and here the power which was essentially the maximum possible power for each reference fuel was measured. The power obtained in operations with pure reference isooctane was adopted as 100%; however, mixtures of isooctane with TES [TEL] made it possible to attain greater power and with an increase in the TES quantity the maximum possible power increased as well.

It was established that pure isooctane has a grading (performance number) of 100, whereas isooctane with 0.76 ml of TES/kg has a performance number of 130, etc.

The fuel grade (performance number) is an indicator of the antiknock property in the case of a rich mixture.

The fuel grade (performance number) shows the extent to which it is possible to produce power (or the mean indicator pressure) in the operation of the special single-cylinder engine on a rich mixture of the fuel being tested in comparison with the power that can be developed by this same engine when it operates on isooctane whose power, when used in this engine, has conventionally been set at 100% and 100 grade units. For example, a performance number of 130 shows that this fuel, in operation in this special single-cylinder engine, provides for an increment of 30% in power in comparison with pure isooctane. The higher the grade of the fuel the better its antiknock properties in the case of rich mixtures under conditions of pressure feed.

DETERMINATION OF THE OCTANE NUMBER IN ACCORDANCE WITH THE MOTOR METHOD

Octane numbers according to the motor method are determined on a single-cylinder IT9-2 installation, following the GOST 511-61 (Fig. 21), which consists of the following basic units:

1) a single-cylinder four-stroke piston engine, liquid cooled, with a variable compression ratio which can range from 4 to 10 during engine operation;

2) and asynchronous electric motor developing 5.8 kw, connected to the piston engine by means of two wedge-like belts, and intended for the maintenance of a constant rpm (900 $\pm$ 10 rpm) during the testing period;

3) a control panel on which are mounted all of the monitoring-measuring instruments and equipment required to control the engine;

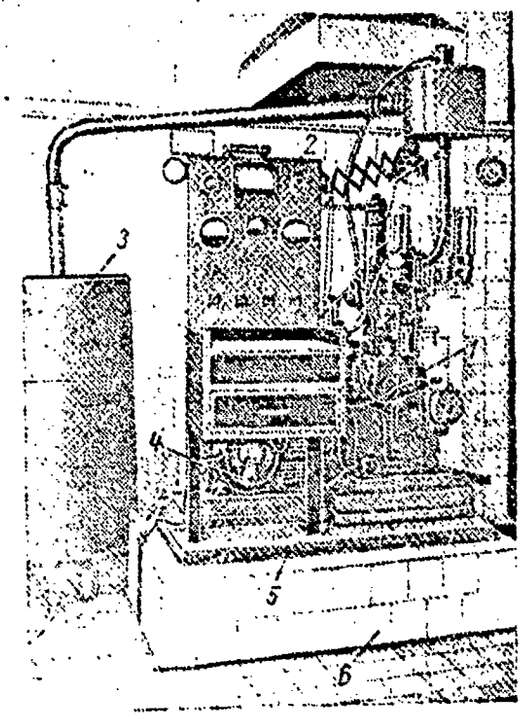


Fig. 21. General view of IT9-2 installation for determination of octane numbers of fuels by the motor method. 1) Single-cylinder engine; 2) control panel; 3) ice column; 4) asynchronous electric motor; 5) cast-iron plate; 6) foundation.

4) equipment for measurement of knock, this equipment consisting of an electromechanical sensing element and an electrical measuring instrument – a detonation (knock) indicator;

5) a flask filled with ice to maintain at constant humidity the air drawn into the engine cylinder.

The basic units of the installation, with the exception of the flask for the ice, are mounted on a massive cast-iron plate.

This single-cylinder piston engine has all of the required units and equipment which make possible the combustion of a fuel in its cylinder, as well as to keep the engine in operation for a long period of time. The variable compression ratio provides for the ability to produce knocking in various fuels – from low-octane tractor kerosenes to the high-octane aviation gasolines.

The installation is equipped with special equipment making it possible to maintain rigorous constant (standard) conditions for the tests: the rpm, the temperature regime, the composition of the working mixture, constant humidity of the air drawn in, standard knock intensity, etc. In recent years the IT9-2 installation has undergone a number of structural changes which serve to improve its operational characteristics. The cylinder clamp has been improved, and a small-scale [illegible] has been installed; a special receiver has been installed in the

haust system. The electrical circuitry of the installation has been simplified, and improved instruments have been installed, etc.

With the motor method, fuel octane numbers are determined for a specified knock intensity.

The equipment employed to measure fuel knock ratings consists of an electromechanical sensing element for knock that is based on the principle of measuring local pressure increases as they occur in the detonation combustion of the fuel.

The electromechanical detonation sensing element (Fig. 22) consists of a steel cylindrical frame in which a steel rod is housed. There is a socket at the bottom part of the frame, into which a thin steel membrane has been pressed. A crossbeam is fastened to the upper part of the frame, and this beam has two spring plates with tungsten contacts, as well as screws to control the spring-plate tension and the clearance between the contacts. The bottom end of the steel rod rests freely against the membrane, and a spring plate with a contact is positioned at the top end of the rod. A rigorously specified clearance (0.10-0.13 mm) is established between the contacts to which a d.c. voltage of 110 v is applied. The sensing element is screwed into the cylin-

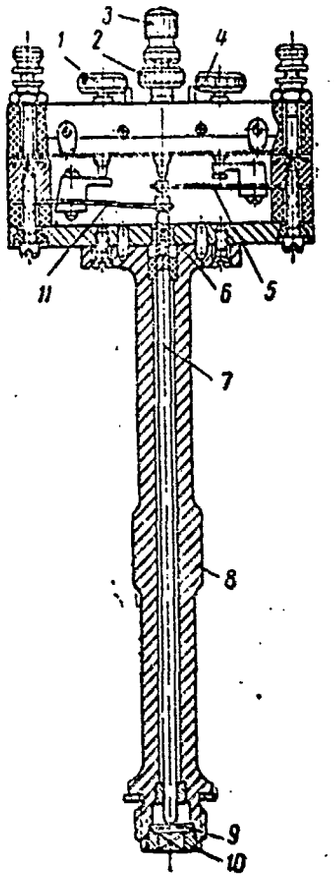


Fig. 22. Electromechanical sensing element for knocking. 1) Screw controlling tension of lower spring plate; 2) central screw for control of clearance between contacts; 3) plunger screw; 4) screw controlling tension of upper spring plate; 5) upper spring plate with contact; 6) ebonite rod tip; 7) steel rod; 8) frame of detonation (knock) sensor; 9) steel diaphragm; 10) nut used to press against membrane; 11) lower spring plate with contact.

der head so as to position the membrane within the combustion chamber.

In the case of detonation combustion of the fuel, the thin steel membrane under the action of the "detonation shocks" (increased local pressures) bends and exerts pressure against a steel core which closes the contacts of the spring plates. With the closing of the contacts, a current passes through the circuit of the detonation sensor (a thermoelement, resistors, and an indicator), and the thermoelement and the detonation (knock) indicator are used to measure the magnitude of this current.

The scale readings of the detonation indicator are functions of time during which the contacts are closed, and this in turn is a function of the knock intensity. The higher the detonation (knock) intensity, the longer the contacts of the sensing element are closed, and the greater the readings of the detonation (knock) indicator.

The method used to determine the octane numbers of fuels involves the following. Given strictly constant engine operating conditions and specific (standard) knock intensity, an equivalent reference fuel is selected for the specimen being tested. An equivalent reference fuel is one which, all other conditions being equal, produces knocking in exactly the same manner and under the identical conditions as does the specimen being tested.

Isooctane and n-heptane are reference fuels, and these are used to prepare mixtures having specific volumetric ratios.

The octane numbers of the reference-fuel mixtures are known, since the percentage of isooctane in these fuels is the octane number.

Because of the great cost of isooctane and normal heptane, secondary reference fuels are used for operations, since these can be calibrated in advance according to the isooctane in mixture with n-hep[illegible], i.e., the octane numbers of the reference fuels are established o[illegible]

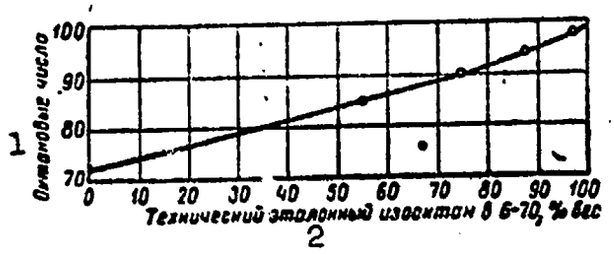


Fig. 23. Scale for conversion of secondary reference fuels to primary reference fuels (to octane numbers). Secondary reference fuel mistures of industrial reference isooctane with B-70 gasoline. 1) Octane numbers; 2) industrial reference isooctane in B-70, % by weight.

taken from a conversion scale by means of which the secondary reference-fuel values are converted to the primary values.

Mixtures of industrial reference isooctane (TEI) with white spirit or B-70 aviation gasoline are used as the secondary reference fuels.

The conversion scale is prepared in the following manner. The mixtures of the primary reference fuels are compared against the mixtures of the secondary reference fuels, i.e., each mixture of primary reference fuel is matched by antiknock properties to a mixture of secondary reference fuels, and this is accomplished on an engine operating under standard conditions and knock intensity.

A graph is prepared on the basis of the derived data, and this graph is referred to as a conversion scale (Fig. 23). Subsequently, the secondary reference fuels and this conversion scale are employed in the daily work of determining fuel octane numbers.

The motor method makes it possible to determine octane numbers within an extremely wide range: from zero to 100 units. Experience in the application of this method has demonstrated that the most exact results are obtained in an interval of 60-90 octane units.

DETERMINATION OF OCTANE NUMBER ACCORDING TO THE RESEARCH METHOD

The determination of octane numbers by the research method is accomplished on a single-cylinder IT9-6 installation in accordance with GOST 8226-61.

Structurally the IT9-6 installation differs little from the single-cylinder IT9-2 installation described above and shown in Fig. 1.

These installations are distinguished on the basis of the conditions under which the tests are carried out, and in the case of the IT9-6 installation these tests are characterized by the following:

1) an engine rpm of 600 rpm, in connection with which a flywheel of smaller diameter is installed on the shaft of the asynchronous electric motor.

2) the crank-angle ignition lag of $13^{\circ}$ before top center is constant for all compression ratios; to achieve this angle, a lever to change the crank-angle ignition lag is installed in the magneto and fixed in a definite position;

3) the fuel-air mixture is not heated, and in this connection the intake system of the engine does not have any connecting pipes leading to an electric heater; the carburetor is connected directly to the intake orifice of the cylinder by means of a ring;

4) with a carburetor setting for maximum knock, the fuel level in the float chamber must range between 0.8 and 2.0 units on the scale; to achieve this, large-diameter (0.9-1.0) jet tubes have been provided;

5) the control and verification of valve clearances are carried out at a compression ratio of 5.9.

In everything else, the research method of determining octane numbers is exactly like the motor method.

Despite these insignificant differences between the motor and research methods, the results obtained in the determination of octane

numbers for various fuels, obtained by these methods, may exhibit substantial discrepancies.

Table 5 shows octane numbers for various gasolines, and these numbers have been determined both according to the research and motor methods. The greatest octane-number difference is found in the case of coking gasolines, as well as gasolines from catalytic cracking and reforming, i.e., these gasolines exhibit the greatest sensitivity. There is a slightly smaller difference between the octane numbers for the thermal-cracking gasolines (average in terms of sensitivity). Direct-distillation gasolines exhibit an insignificant difference with respect to octane numbers determined by these methods, and such gasolines are regarded as insensitive or low-sensitivity fuels.

TABLE 5

Octane Numbers for Various Gasolines According to the Research and Motor Methods

| 1 Топливо | 2 Октановое число | | 5 Чувствительность (ис-им) |
|---|---|---|---|
| | 3 Исследовательский метод (ис) | 4 моторный метод (им) | |
| 6 *Бензины прямой перегонки* | | | |
| 7 Бакинской нефти | 69.0 | 66.0 | 2.0 |
| 8 Грозненской нефти (к. к. 120°) | 71.0 | 70.0 | 1.0 |
| 9 Краснокамской нефти | 71.0 | 70.0 | 1.0 |
| 10 Ухтинской нефти | 51.4 | 48.8 | 2.6 |
| 11 Бугурусланской девонской нефти (к. к. 85°) | 62.0 | 64.0 | —2.0 |
| 12 Жирновской нефти (к. к. 153°) | 78.0 | 75.9 | 2.1 |
| 13 Пермской нефти | 61.8 | 58.8 | 3.0 |
| 14 Ханжинской нефти (к. к. 164°) | 66.6 | 64.3 | 2.3 |
| 15 Среднеазиатской нефти | 58.0 | 55.0 | 3.0 |
| 16 Ромашкинской нефти (к. к. 55°) | 64.4 | 66.0 | —1.6 |
| 17 Пермской нефти (к. к. 170°) | 51.0 | 51.3 | —0.3 |
| 18 *Бензины термического крекинга* | | | |
| 19 Нефтяное сырье | 77.6 | 71.0 | 6.6 |
| » | 76.6 | 69.8 | 7.2 |
| 20 Парафиновое сырье | 70.0 | 64.7 | 5.3 |
| » | 72.0 | 66.4 | 5.6 |
| » | 70.9 | 65.2 | 5.7 |

[TABLE 5 Cont'd]

| | | | |
|---|---|---|---|
| 21 *Бензины каталитического крекинга* | | | |
| 22 Тяжелого сырья ромашкинской нефти . . . . . | 83,8 | 76,2 | 7,6 |
| 23 Тяжелого сырья туймазинской девонской нефти . . . . . | 87,0 | 77,8 | 9,2 |
| 24 Бензин каталитического риформинга | 3,6 | 77,0 | 6,6 |
| 25 Бензин коксования . . . . . | 84,0 | 69,8 | 14,2 |

1) Fuel; 2) octane number; 3) research method (imep); 4) motor method (mm); 5) sensitivity (imep – mm); 6) direct-distillation gasolines; 7) Baku petroleum; 8) Groznyy petroleum (start of boiling, 120°); 9) Krasnokamsk petroleum; 10) Mukhanovo petroleum; 11) Tuymazy devonian petroleum (start of boiling at 85°); 12) Zhirnovsk petroleum (start of boiling at 153°); 13) Il'skiy petroleum; 14) Khadyzhensk petroleum (start of boiling at 164°); 15) Central Asian petroleum; 16) Romashkinskiy [sic] (start of boiling at 85°); 17) Perm' petroleum (start of boiling at 170°); 18) thermal-cracking gasolines; 19) naphthenic crude; 20) paraffinic crude; 21) catalytic,cracking gasolines; 22) heavy crude of Romashkinskiy petroleum; 23) heavy crude of Tuymazy devonian petroleum; 24) catalytic reforming gasoline; 25) coking gasoline.

MIXING OCTANE NUMBER

In determining fuel octane numbers by the motor and research methods it is sometimes impossible to test a given product directly in the engine for the following reasons:

1) the product to be tested is higher than the reference isooctane or lower than the n-heptane in terms of antiknock properties;

2) the product being tested does not correspond, in terms of volatility, to the conditions of carburetion (it is somewhat too volatile or vaporizes poorly);

3) there is an inadequate quantity of the product for testing purposes.

In such cases the antiknock property is determined by mixing the product being tested with the reference gasoline whose octane num-

is either known or can be determined.

The mixing octane number is determined in the following manner. A mixture of the fuel being tested with the reference fuel (desirably in a 1:1 ratio) is prepared. This mixture is then tested in the conventional manner in the installation in order to determine the octane number. On the basis of the obtained results, the following formula is employed to compute the octane number of the product being tested:

$$x = \frac{100C - y(100 - a)}{a},$$

where x is the mixing octane number; y is the octane number of the reference fuel used for purposes of mixing; a is the content of the fuel being tested, in the reference fuel, in %; C is the octane number of the mixture.

If the octane numbers of the initial components are known, the following formula can be used to determine the percentage relationships of these components in the binary mixture and to obtain the given octane number of the mixture:

$$a = 100\,\frac{C - B}{A - B},$$

where a is the content of the first component in the mixture, in %; A is the octane number of the first component; B is the octane number of the third component; C is the required (given) octane number of the mixture.

In the practice of compounding gasolines, the method of calculating the mixing octane number and the percentage content of the components in the mixture is frequently employed.

The mixing octane numbers, in comparison to the actual octane numbers, i.e., the numbers obtained in the direct determination of octane numbers on the installation by the motor method, showed the following:

1. Direct-distillation gasolines and paraffinic hydrocarbons behave additively in the mixture, i.e., the mixing (mixture) octane numbers correspond to the octane numbers obtained in the determination in the [test] installation.

2. The mixing (mixture) octane numbers for the thermal- and catalytic-cracking gasolines, and those for the olefinic hydrocarbons in mixture with direct-distillation gasolines come out lower than the octane numbers determined directly in the installation, i.e., the octane numbers of the mixtures which contain these gasolines are actually higher than when these octane numbers are calculated on the basis of the octane numbers of the initial components.

3. The mixing (mixture) octane numbers for aromatic hydrocarbons and components are higher than in the direct determination in the installation. With an increase in the content of aromatic hydrocarbons in the mixture, the discrepancy increases and reaches as high as 8-10 octane units.

DETERMINATION OF ANTIKNOCK VALUES OF GASOLINES AND COMPONENTS WITH OCTANE NUMBERS HIGHER THAN 100.

Both the motor and research methods of determining octane numbers make it possible to evaluate fuels exhibiting antiknock values below 100 octane units.

In evaluating fuels with octane numbers in excess of 100, we use the method of mixing the fuels with low-octane reference gasoline and the antiknock property is, in this case, expressed in mixing (mixture) octane numbers. This complicates the process of determining the octane number and frequently distorts the true octane number of the high-octane fuel or component.

In actual practice there exist various methods of determining oc-

TABLE 6

Octane Numbers of Chemically Pure Isooctane with Various TES [TEL] Content

| 1 Содержание ТЭС в химически чистом изооктане, мл/кг | 2 Октановое число | Содержание ТЭС в химически чистом изооктане, мл/кг | Октановое число | Содержание ТЭС в химически чистом изооктане, мл/кг | Октановое число |
|---|---|---|---|---|---|
| 0,05 | 101,6 | 0,60 | 111,2 | 1,30 | 116,4 |
| 0,10 | 103,1 | 0,65 | 111,7 | 1,40 | 116,9 |
| 0,15 | 104,3 | 0,70 | 112,2 | 1,50 | 117,4 |
| 0,20 | 105,4 | 0,75 | 112,7 | 1,60 | 117,8 |
| 0,25 | 106,4 | 0,80 | 113,0 | 1,70 | 118,2 |
| 0,30 | 107,3 | 0,85 | 113,5 | 1,80 | 118,6 |
| 0,35 | 108,1 | 0,90 | 113,9 | 1,90 | 119,0 |
| 0,40 | 108,8 | 0,95 | 114,2 | 2,00 | 119,4 |
| 0,45 | 109,5 | 1,00 | 114,6 | 2,10 | 119,7 |
| 0,50 | 110,0 | 1,10 | 115,2 | 2,20 | 120,0 |
| 0,55 | 110,7 | 1,20 | 115,8 | 2,30 | 120,3 |

1) TES [TEL] content in chemically pure isooctane, ml/kg; 2) octane number.

tane numbers in excess of 100 and these, in principle, can be divided into two basic groups.

1. The methods based on the utilization of reference fuels exhibiting antiknock values in excess of chemically pure isooctane, i.e., in excess of 100 octane units (ethylated isooctane, ethylated triptane (2,2,3-trimethylbutane) and their mixtures with n-heptane, etc.)

2. The methods of calculating octane numbers according to formulas based on the extrapolation of the octane-number scale above 100 units. To determine fuel octane numbers above 100 by the motor and research methods, the most common practice is to use the scale constructed according to the Vize [sic] formula (proposed by "The General Motors Research Corporation")

$$\text{О. Ч.} = 100 + \frac{N - 100}{3},$$

where N is the performance number of chemically pure isooctane containing the various quantities of TES [TEL], in ml/kg.

TABLE 7

Octane Numbers of Fuels, Higher than 100 on the Scale (Data after Ye.I. Zabryanskiy and Yu.A. Robert)

| 1 Топливо | 2 Октановое число | | 5 Чувствительность (пм — мм) |
|---|---|---|---|
| | 3 исследовательский метод | 4 моторный метод | |
| 6 Бензол | 113,0 | 106,4 | 6,6 |
| 7 Толуол | 115,7 | 104,2 | 11,5 |
| 8 Изопропилбензол | 108,0 | 96,0 | 12,0 |
| 9 Авиабензин БА | 109,5 | 104,4 | 5,1 |
| 10 Авиаалкилат Р-9, *мл/кг*: | | | |
| 1,0 | 101,6 | 101,7 | —0,1 |
| 2,0 | 105,6 | 104,2 | 1,4 |
| 3,0 | 108,2 | 107,2 | 1,0 |
| 11 Контрольное топливо № 8 (Б-100/130) | 101,5 | 99,2 | 2,3 |
| 12 Диизобутилен | 100,4 | 85,0 | 15,4 |

1) Fuel; 2) octane number; 3) research method; 4) motor method; 5) sensitivity (imep – mm); 6) benzene; 7) toluene; 8) isopropylbenzene; 9) BA aviation gasoline; 10) Aviation alkylate R-9, ml/kg; 11) control fuel No. 8 (B-100/130); 12) diisobutylene.

The calculation of the octane numbers of isooctane with a TES [TEL] content ranging from 0.05 to 2.3 ml/kg (Table 6) was carried out in accordance with this formula.

The conditions for the determination of octane numbers in excess of 100 in motor- and research-method installations are in complete accord with the conditions for the determination of octane numbers below 100, with the sole exception that mixtures of chemically pure isooctane with various TES [TEL] contents are employed as the reference fuels.

An equivalent reference fuel – isooctane + TES [TEL] – is selected for the specimen being tested, and for the reference fuel a corresponding octane-number value is found in Table 6.

Example. As a result of the determination it was found that the specimen being tested was equal, with respect to knock intensity, to isooctane with a TES [TEL] content of 0.50 ml/kg. The above-indicated

mixture has an octane number of 110.0 in accordance with Table 5. This means that the specimen being tested has an octane number of 110.0.

The tests that were carried out at the VNII NP [All-Union Scientific Research Institute for the Processing (Refining) of Petroleum and Gas and for the Production of Synthetic Liquid Fuel] as well as by other organizations, demonstrated that the above-indicated method for the determination of octane numbers above 100 makes it possible to determine with sufficient accuracy the antiknock properties of high-octane fuels and components by both the motor and research methods (Table 7).

DETERMINATION OF RICH-MIXTURE AVIATION-GASOLINE GRADES

The grade of an aviation gasoline is determined by means of a single-cylinder IT9-1 installation in accordance with GOST 3338-61 (Fig. 24).

During the test, the engine of this installation operates in a forced regime (see Table 3) and with pressure-feed of compressed air into the engine cylinder, which comes very close to producing the actual operating conditions of piston aviation engines.

The IT9-1 installation is equipped with certain structural features which distinguish it significantly from those installations employed to carry out tests in accordance with the motor and research methods. Of these the basic features are the following: the single-cylinder engine is equipped with a pressure-feed system, and instead of a carburetor, for purposes of preparing the working mixture a single-plunger pump and a spray nozzle have been installed. The fuel is sprayed into the stream of compressed and heated air in the intake system by means of this spray nozzle. The fuel flow rate is measured by means of scales, and the measurement of the air flow

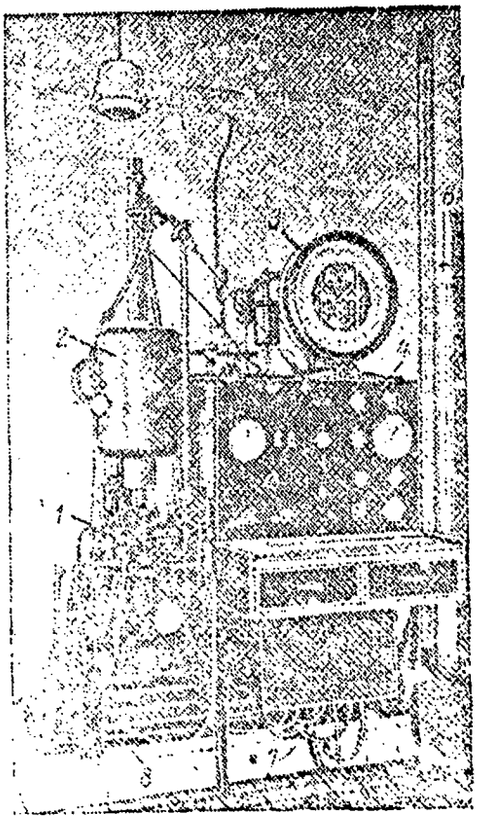

Fig. 24. Over-all view of IT9-1 installation for determination of rich-mixture aviation-gasoline grades. 1) Single-cylinder engine; 2) small receiver of engine's system; 3) dynamometer for measurement of mean indicator pressure ($p_i$); 4) control panel; 5) manometer for measurement of feed pressure; 6) manometer for measurement of air flow rate; 7) foundation (base) of installation; 8) cast-iron plate.

rate is accomplished by means of a measurement plate. The belt-drive single-cylinder engine is connected to an electric-motor-generator developing a power of 25 kw which is balanced on bearings and has a lever system for the measurement of the mean effective and mean friction pressure (apparatus for the measurement of engine power). This device makes it possible to maintain a constant rpm for the single-cylinder engine throughout the test and to determine the mean indicator pressure ($p_i$).

Testing in accordance with this method involves the determination of knock characteristics for the fuels and reference fuels being tested, and these are relationships between the mean indicator pressure ($p_i$) and the composition of the mixture ($\lambda$) when the engine operates in a regime of light (initial) knocking. A light (or initial) knocking regime is attained by varying the pressure feed.

The mean indicator pressure is measured by means of a scale-dynamometer in the following manner. When the single-cylinder engine is operating on a particular fuel, the indicator (arrow) of the dynamometer indicates the mean effective pressure. With cessation of

feed and rotation of the single-cylinder engine by means of the electric motor, the indicator of the dynamometer points to the mean friction pressure. The sum of these two mean pressures makes up the mean indicator pressure, i.e.,

$$p_i = p_e + p_r,$$

where $p_i$ is the mean indicator pressure; $p_e$ is the mean effective pressure; $p_r$ is the mean friction pressure.

The composition of the working mixture is determined by the following formula:

$$\lambda = \frac{g_t}{g_v},$$

where $\lambda$ is the composition of the working mixture ($\lambda$ is the reciprocal of $\alpha$); $g_t$ is the fuel flow rate, in kg/hr; $g_v$ is the air flow rate, in kg/hr.

The magnitudes of $g_t$ and $g_v$ are measured during the test.

During the research and experimental work, the total knocking characteristic of the fuel is generally determined for a wide range of changes in the composition of the working mixture ($\lambda = 0.055 - 0.12$ or $\alpha = 1.2 - 0.55$). In this case, 7-8 points are determined (Fig. 35).

To determine the fuel grade, 4-5 points are determined for the rich-mixture regions alone ($\lambda = 0.07 - 0.12$).

In the determination of each point of the knocking characteristic the composition of the working mixture ($\lambda$) is established and the mean indicator pressure ($p_i$) developed during the combustion of this mixture in the engine cylinder in a regime of light (or initial) knocking is measured.

The results obtained in the determination of the knocking characteristics of the fuels being tested are plotted on a special graph of standard curves taken from the reference fuels, and here the composi-

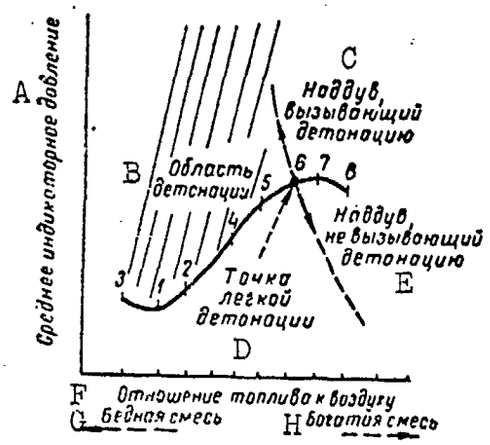


Fig. 25. Graph for determination of points of total fuel knocking characteristic on IT9-1 installation. A) Mean indicator pressure; B) knocking region; C) pressure feed resulting in knocking; D) point of light knocking; E) pressure feed not producing knocking; F) fuel-to-air ratio; G) lean mixture; H) rich mixture.

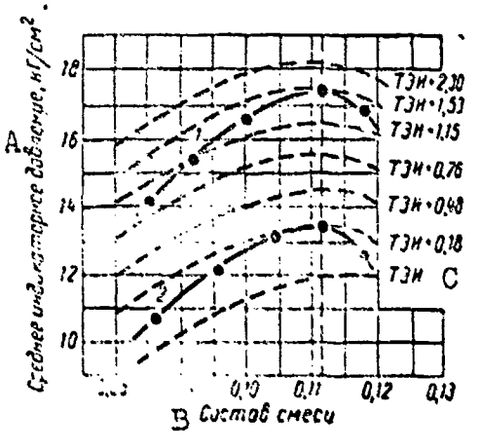


Fig. 26. Grid for standard detonation characteristics of reference fuels. 1 and 2 are the detonation (knocking) characteristics of the fuels being tested. A) Mean indicator pressure, kgf/cm$^2$; B) composition of mixture; C) TEI.

tion of the working mixture ($\lambda$ = = 0.55 - 0.13) is plotted along the axis of abscissas, and the mean indicator pressure ($p_i$ = 6 - 18 kg-force/cm$^2$) is plotted along the axis of ordinates.

The graph for the standard knock characteristics of the reference fuels is uniform for all IT9-1 installations (Fig. 26); this graph includes the characteristics for seven reference fuels for which the grades (performance numbers) have been established.

Industrial reference isooctane (TEI) with a motor-method octane number of 98-99 is employed as the reference fuel, as are mixtures of industrial reference isooctane with tetraethyllead (TES [TEL]) in the form of an ethyl fluid.

After the determination of the points with the fuel being tested, and after these points have been plotted on the graph of standard characteristics, a determination is made of the reference-fuel characteristic which corresponds to the fuel being tested in terms of the maximum [illegible]

TABLE 8

Magnitude of Fuel Grade as a Function of Reference Mean Indicator Pressure (Reference $p_i$)

| 1 $p_i$ (приведенное), кГ/см² | 2 Сортность | $p_i$ (приведенное), кГ/см² | Сортность | $p_i$ (приведенное), кГ/см² | Сортность |
|---|---|---|---|---|---|
| 11,9 | 100 | 13,6 | 121 | 15,8 | 142 |
| 12,0 | 101 | 13,7 | 122 | 15,9 | 143 |
| 12,05 | 102 | 13,8 | 123 | 16,0 | 144 |
| 12,1 | 103 | 13,85 | 124 | 16,2 | 145 |
| 12,2 | 104 | 13,9 | 125 | 16,3 | 146 |
| 12,3 | 105 | 14,0 | 126 | 16,4 | 147 |
| 12,4 | 106 | 14,1 | 127 | 16,6 | 148 |
| 12,45 | 107 | 14,2 | 128 | 16,7 | 149 |
| 12,5 | 108 | 14,3 | 129 | 16,9 | 150 |
| 12,6 | 109 | 14,4 | 130 | 17,0 | 151 |
| 12,7 | 110 | 14,5 | 131 | 17,2 | 152 |
| 12,8 | 111 | 14,6 | 132 | 17,3 | 153 |
| 12,9 | 112 | 14,7 | 133 | 17,4 | 154 |
| 12,95 | 113 | 14,8 | 134 | 17,5 | 155 |
| 13,0 | 114 | 14,9 | 135 | 17,7 | 156 |
| 13,1 | 115 | 15,1 | 136 | 17,8 | 157 |
| 13,2 | 116 | 15,2 | 137 | 17,9 | 158 |
| 13,3 | 117 | 15,3 | 138 | 17,95 | 159 |
| 13,4 | 118 | 15,4 | 139 | 18,05 | 160 |
| 13,45 | 119 | 15,5 | 140 | 18,1 | 161 |
| 13,5 | 120 | 15,7 | 141 | | |

1) $p_i$ (reference), kg-force/cm$^2$; 2) grade (performance number).

cator-pressure value. This reference-fuel characteristic is also used to carry out an evaluation of the fuel being tested.

Examples (see Fig. 26). 1. The fuel being tested (curve 2) in terms of maximum mean-indicator pressure ($p_i$ = 13.26 kg-force/cm$^2$) corresponds to the reference-fuel characteristic for TEI + 0.18 ml/kg TES [TEL] which has a performance number (grade) of 116. Consequently, the fuel has a performance number (grade) of 116.

2. The tested fuel (curve 1) corresponds to the reference-fuel characteristic for TEI + 1.53 ml/kg TES [TEL] which has a performance number of 153. Consequently, the fuel has a performance number of 153.

The grade (performance number) of the fuel being tested can be determined on the basis of the magnitude of the mean indicator pressure ($p_i$) obtained with this fuel, in accordance with Table 8. Therefore, if the tested specimen of commercial fuel does not correspond, in terms of maximum mean indicator pressure ($p_i$), to one of the char-

acteristics for the reference-fuels, i.e., it lies between two adjacent characteristics (reference fuels), the performance number of the given specimen can be found from Table 8 according to the maximum value of $p_i$.

Example. The maximum value of $p_i = 13.5$ kg/cm$^2$ for the tested specimen, which according to Table 8 corresponds to a performance number of 120.

The final results, obtained on the IT9-1 installation, in the evaluation of antiknock properties of fuels can be expressed in various units: TEI + n ml/kg TES [TEL], performance numbers, index number, octane number; most frequently they are expressed in performance-number units, and sometimes in terms of index numbers.

The grade (performance number) of a fuel is referred to as an index of its antiknock property in the case of a rich mixture ($\lambda = 0.112$) which is numerically equal to the performance number (grade) of a reference fuel which when tested on a single-cylinder engine under pressure-feed conditions and a regime of light knocking produces the identical maximum value of the mean indicator pressure as the fuel being tested.

The higher the grade (performance number) of the fuel, the better the antiknock properties it exhibits in the case of rich mixtures under pressure-feed conditions.

Index Number

To evaluate the antiknock properties of fuels and particularly of individual hydrocarbons having a grade (performance number) below 100 or above 160 units, certain conventional units have been adopted and these are referred to as index numbers which characterize antiknock properties of rich-mixture fuels.

Index numbers are determined on the basis of the maximum

the mean indicator pressure from a special table or they are calculated in accordance with the following empirical formula:

$$\text{I. Ch.} = 276 - \frac{29\,650}{p_i},$$

where I. Ch. is the index number of the fuel being tested; $p_i$ is the mean indicator pressure obtained in testing of a specimen on an IT9-1 installation.

Within a range of 100-160 units, the index numbers are insignificantly different from performance-number units; it can be stated that they are virtually equal in this range (since the difference amounts to 1-2 units).

EVALUATION OF AUTOIGNITION PROPERTIES OF DIESEL FUELS

Unlike piston carburetor engines with spark ignition, in engines in which autoignition is achieved as a result of compression the fuel is sprayed directly into the combustion chamber where it ignites under the action of high temperature and air pressure.

In high-speed engines with autoignition as a result of compression, the time required for the preparation and combustion of the fuel is measured in thousands of a second; therefore in order to provide for the normal operation of these engines, the fuel must exhibit certain definite motor properties.

One of the basic indicators which characterize the motor properties of diesel fuels is autoignition. Autoignition of vaporized diesel fuels is of great practical significance.

When a fuel is injected (sprayed) into a medium of hot compressed air contained in the engine cylinder, we can always observe a certain time interval which is measured from the instant of fuel injection to the start of combustion, and this time interval is referred to as the autoignition lag (the period of ignition lag). The shorter this inter-

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val, the better the conditions provided for engine operation.

The autoignition lag and autoignition temperature are primarily functions of the chemical composition of the diesel fuel; they are of significance in the starting of a cold engine and exert considerable influence on the combustion process.

The basic indicator which characterizes the autoignition properties of diesel fuels in an engine cylinder is the cetane number. The evaluation of autoignition properties of diesel fuels, expressed in cetane numbers, gained widespread acceptance.

The cetane numbers of diesel fuels are determined in a special single-cylinder engine in which autoignition is accomplished by compression, and this engine is outfitted with the required apparatus and equipment for the above-indicated purposes. The principle behind the determination of the cetane number is the same as in the determination of octane numbers, i.e., the specimen being tested is compared against reference fuels whose cetane numbers are known.

Cetane ($C_{16}H_{34}$, n-hexadecane) and α-methylnaphthalene ($C_{11}H_{10}$) are used as the primary reference fuels. It has conventionally been agreed that easily ignitible cetane has a cetane numberof 100, whereas α-methylnaphthalene, which has poor ignition properties, has a cetane number of zero.

By preparing a mixture of cetane with α-methylnaphthalene (in %, by volume), it is possible to prepare reference fuels having cetane numbers ranging from zero to 100. The percentage (by volume) of cetane in mixture with α-methylnaphthalene will serve as the cetane number of the mixture.

For example, a mixture of 40% cetane + 60% α-methylnaphthalene has a cetane number of 40.

The cetane number of a diesel fuel is the percentage (by vo

content of cetane in such a mixture with -methylnaphthalene which in terms of ignition properties in the cylinder of the special single-cylinder engine, under standard test conditions, is equal (corresponds) to the specimen being tested. The higher the cetane number of the diesel fuel, the earlier will the fuel ignite in the engine cylinder, and the increase in pressure during the combustion process will be more uniform, and the operation of the engine will be "softer" and, conversely, the lower the cetane number of the diesel fuel, the later will ignition take place, the pressure will rise more sharply as a result of the instantaneous combustion of increased quantities of fuel, and the operation of the engine will be "hard." However, it should be pointed out that "hard" engine operation with compression-ignition, accompanied by knocking, is a function not only of fuel quality but of a series of structural and operational factors as well.

To a great extent such important operational characteristics as ease of cold-engine start, smoothness of combustion process, and fuel flow rate, are functions of the cetane number of the fuel.

With an increase in the cetane number, the time required to start an engine diminishes; for example, in the case of a fuel having a cetane number of 53.0 the time required to start the engine is 3 seconds, whereas in the case of a fuel having a cetane number of 38.0 the time required to start the engine ranges from 45 to 50 seconds. The higher the rpm of the engine, the greater the cetane number required for the fuel. In the case of engine operation on a fuel having a cetane number of 63.0, depending on the type of engine, the specific fuel consumption will be 187-246 g/hp·hr, whereas in the case of a fuel with a cetane number of 39.0 the fuel consumption (flow rate) will be 193-254 g/hp·hr.

The cetane numbers are extremely convenient indicators for the

classification of commercial diesel fuels.

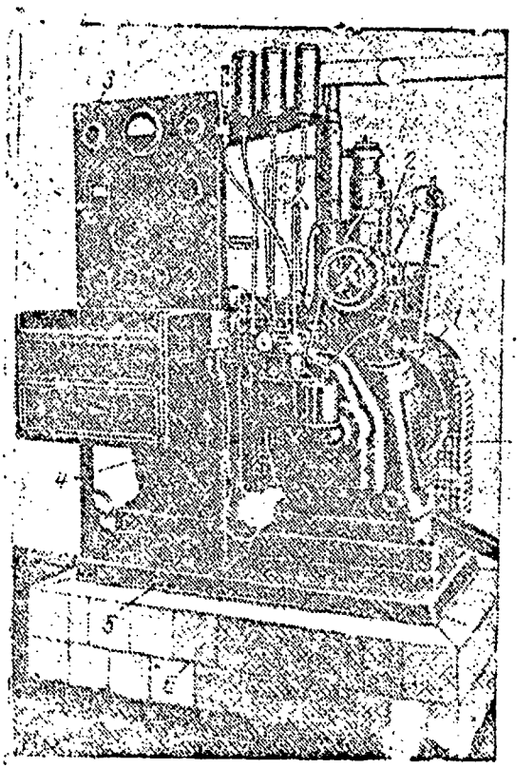

Fig. 27. Over-all view of IT9-3 installation for determination of cetane numbers of diesel fuels, according to the method of flash coincidence. 1) Single-cylinder engine; 2) mechanism for change of compression ratio; 3) control panel; 4) asynchronous electric motor; 5) cast-iron plate; 6) foundation (base).

There are a number of methods for the determination of diesel-fuel cetane numbers. Formerly, the method of the critical compression ratio (and the method of ignition lag) were employed for this purpose. More recently, a flash-coincidence method has been devised, and this method gained widespread acceptance.

The Flash-Coincidence Method

Cetane numbers of diesel fuels are determined by the flash-coincidence method in accordance with GOST 3122-52 on a single-cylinder IT9-3 installation (Fig. 27), and this installation contains the following basic units.

1. A single-cylinder four-stroke engine of the antechamber type with compression-autoignition and a variable compression ratio (which is altered by the shifting of a small piston in the antechamber), and which can change during engine operation within a range of from 7 to 23.

2. An electric-motor-generator of the asynchronous type, developing a power of 7 kw, which is connected by means of two wedge-like belts to the flywheel of the single-cylinder engine and is intended to stop this engine, decelerate it, and provide for a constant rpm throughout the test.

3. A control panel on which are mounted all monitoring-measuri

instruments and equipment to control the engine.

4. The fuel equipment consisting of a single-plunger pump, a closed-type pin spray nozzle, tanks, and the fuel system.

5. Equipment which controls the injection and ignition of the fuel, said equipment consisting of an injection (spray) indicator (Fig. 28) (crossbeams, an electromechanical knock sensing element), connected to the spray nozzle, and an electromechanical ignition indicator that is screwed into the combustion chamber (antechamber) of the engine (Fig. 29).

In addition, the flywheel of the engine has a special device with two electronic neon bulbs which are separated from one another along the rotation path by 13°; forward along the rotation path of the crankshaft we find a neon bulb that is connected by means of an electric lead to the injection (spray) indicator, and beyond this bulb it is connected with the ignition indicator. Above the flywheel a special viewing tube with sighting crosshairs is mounted on a bracket.

Essentially, the determination of the cetane number by this method involves the comparison, in an engine operating under rigorously controlled conditions, of the fuel specimen being tested against the reference fuels whose cetane numbers are known.

The determination is carried out with a compression ratio (the determinations are made on the basis of the flash-coincidence of the neon lights on the flywheel) at which fuel autoignition in the combustion chamber takes place at top dead center with a constant spray (injection) angle equal to 13° before top center.

The method used to test the fuels is the following. In spraying the fuel into the antechamber of the engine operating under constant conditions, the pin of the spray nozzle is raised by the fuel pressure and this pin closes the contacts of the spray (injection) indicator as

a result of which the first neon light on the flywheel lights up. If the fuel spray (injection) takes place beyond 13° before top center, the light will flash exactly opposite the crosshair of the viewing tube and will continue to glow the entire time, until the spray-nozzle pin is lifted (the duration of fuel injection). In the field of view of the operator looking through the viewing tube there appears a long strip of red light which begins exactly beneath the crosshair.

The clearance between the contacts of the ignition indicator, installed in the antechamber of the engine, is so regulated as to have the contacts close at the instant of fuel flashing. At the instant of flashing (ignition) of the fuel, the second neon light on the flywheel goes on and parallel glowing red bands can be seen in the viewing tube. The second glowing band must also begin exactly at the viewing crosshairs. As a result, the compression ratio is changed.

If the compression ratio for the fuel being tested is selected properly and if both of the red bands of light begin strictly beneath the viewing crosshairs of the viewing tube, i.e., if they coincide, then a reference fuel is selected so as to provide for the coincidence of the flashes (of the neon light on the flywheel) for the compression ratio found for the fuel specimen being tested.

As in all of the previous methods, for the daily work of determining cetane numbers we use secondary reference fuels (gas oil and green oil) which are preliminarily calibrated according to primary reference fuels. The calibration results are gathered into the form of the graph of the conversion scale shown in Fig. 30.

Diesel-fuel cetane numbers are functions primarily of the chemical composition of the fuel. The highest cetane number (the best ignition properties) are exhibited by paraffinic hydrocarbons. Aromatic hydrocarbons are the poorest fuels for compression-ignition engines, since

they have the lowest cetane numbers. Naphthenic hydrocarbons occupy an intermediate position. Since 1961, a modernized IT9-3M installation is being produced, and in terms of equipment this installation is a definite improvement. The design of the compression-ratio-change mechanism on this installation has been improved. The exhaust system has been fitted out with a special receiver. The d.c. generator has been replaced by a current rectifier. Improved instruments have been installed, etc.

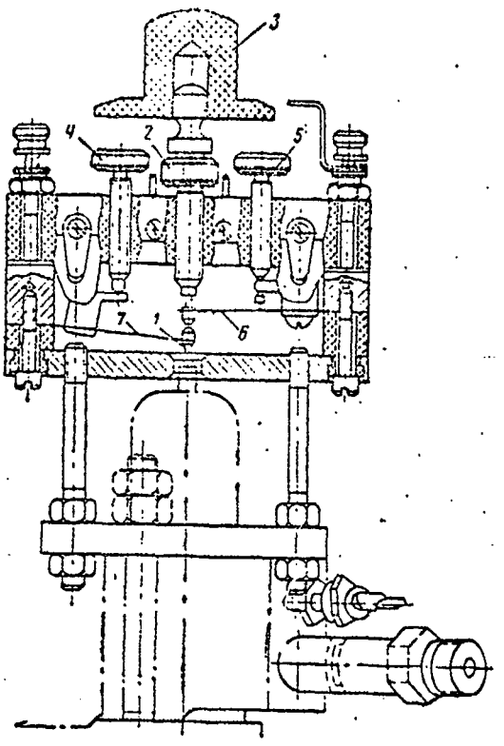


Fig. 28. Electromechanical injection (spray) indicator (cross-beam of detonation (knocking) sensing element). 1) Shaft of spray-nozzle pin; 2) central screw for control of clearance between contacts; 3) bakelite head of central plunger; 4) screw for control of the tension of the lower spring plate; 5) screw for control of the tension of upper spring plate; 6) upper spring plate with contact; 7) lower spring plate with contact.

DETERMINATION OF ANTIKNOCK PROPERTIES OF FUELS ABROAD

In the Peoples' Democracies the IT-9 installation is used predominantly for the determination of the antiknock properties of gasolines and the ignition properties of diesel fuels. In many countries (USA, Great Britain, France, Italy, Iran, etc.) the ASTM-CFR installations are used, and these are produced by the American firm of "Waukesha Motor Company." This firm is presently producing five various types of single-cylinder installations:

1) for the determination of the octane numbers of automotive and aviation gasolines according to the motor method (standard D-357);

2) for the determination of octane numbers of automotive gasolines

by the research method (standard D-908);

3) for the determination of the antiknock properties of high-octane aviation gasolines by the 1c method (standard D-614);

4) for the determination of performance numbers for rich-mixture aviation gasolines by the 3c method (standard D-909);

5) for the determination of the cetane numbers of diesel fuels by the flash-coincidence method (standard D-613).

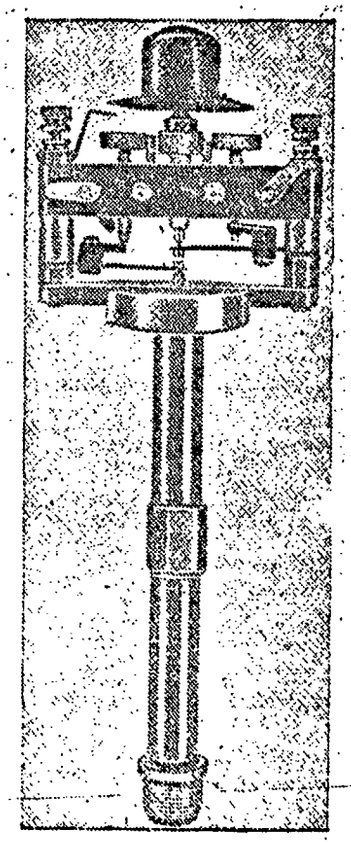

Fig. 29. Electromechanical ignition indicator (a type of knock sensing element).

Each of the above-enumerated ASTM-CFR installations is a specially equipped laboratory motor stand of almost the same type as the IT-9 installation which consists of a single-cylinder engine with a variable compression ratio, a synchronous electric motor connected to the engine, a control panel with monitoring-measuring equipment, and the instruments required for the carrying out of the tests. The ASTM-CFR installations all use similar single-cylinder engines which exhibit the following basic technical characteristics: cylinder diameter 82.6 mm; piston stroke 114.3 mm; working volume of cylinder, 0.612 liters.

In recent years, a number of improvements and changes have been introduced into the single-cylinder ASTM-CFR installations, as well as into the conditions under which the fuel tests in these installations are carried out, and as a result contemporary installations are substantially different from those produced earlier (Fig. 31). The system of spent-gas exhaust from the engines by means of an expansion-receiver installation for reduction of exhaust counterpressure has been improved on all

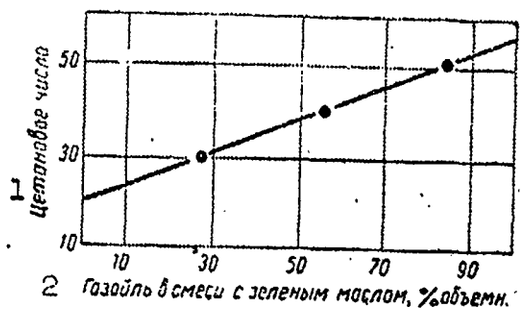


Fig. 30. Scale for conversion from secondary reference fuels to primary reference fuels, in the determination of cetane numbers. 1) Cetane number; 2) gas oil in mixture with green oil, %, by volume.

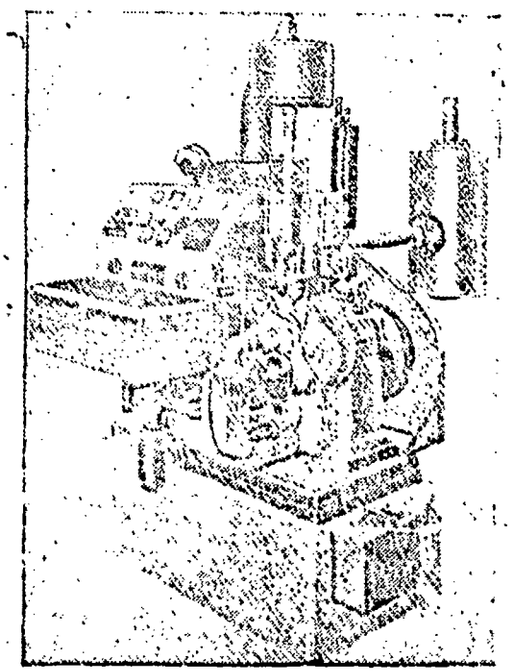

Fig. 31. Over-all view of ASTM-CFR installation (Waukesha) for determination of octane numbers by the research method.

types of installations.

In the installations employed for methods 1c and 3c this receiver provides for special water cooling of the spent gases.

In the installations employed for the motor and research methods, as well as in the installation employed for the 1c method, the diameter of the air intake tube in the column has been substantially increased in order to maintain constant humidity for the intake air, and this substantially reduces the intake resistance.

In the installations employed in the motor and research methods, instead of the Midzhley [sic] pin and "knock-meter" for the measurement of knock intensity, we use an electronic detonometer, i.e., the "Phillips" (model 501A) with a magnetostrictive D-1 sensing element, in connection with which there have been changes introduced into the design of the control panel and the distribution of the instruments and equipment on the control panel, as may be seen in Fig. 31.

The utilization of this equipment has no effect on the magnitude of the antiknock property estimate, but substantially facilitates and

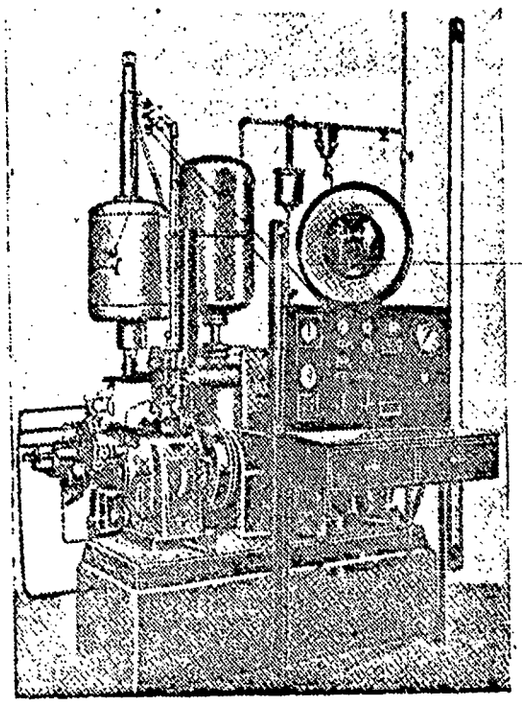

Fig. 32. Over-all view of ASTM-CFR installation (Waukesha) for determination of aviation-gasoline performance number by the 3c method.

and accelerates the determination, and also makes possible greater accuracy and reliability in the results obtained.

In the ASTM-CFR installation for the 3c method for the evaluation of knock intensity, we use the Sperry detonometer (model KM-1) with a magnetic vibration-frequency sensing element. In addition, other improvements have been introduced into this design. For example, the single-cylinder engine is connected to the synchronous electric motor by means of a special clutch rather than by means of the belt drive. As a result the losses due to friction have been reduced and the possible slipping of the belt has been eliminated. The position of the air receivers in the compressed-air system (pressure feed) has been changed. The air receivers have been installed vertically, one above the other. Both of these improvements served to make this a more compact installation (Fig. 32).

In addition to the above-enumerated substantial changes in the design of the single-cylinder ASTM-CFR installations, other less significant improvements have also been introduced.

The following changes have been introduced into the conditions required for the execution of the fuel tests in ASTM-CFR installations. For the daily checking of the proper functioning of the installations (for the motor and research methods, as well as for methods 1c and 3c)

in addition to reference fuels, use is also made of special control fuels consisting of mixtures of individual hydrocarbons of isooctane with n-heptane, containing ethyl fluid (0.53 ml/kg TES [TEL]).

To prepare the grid of standard knocking characteristics by the 3c method, instead of the industrial reference isooctane (fuel S), chemically pure reference isooctane (2, 2, 4-trimethylpentane) is used. In this connection, the magnitude of the mean indicator pressure ($p_i$) of the knocking characteristics of all the reference-fuel curves (the standard grid of reference-fuel curves) has been reduced somewhat. In the remainder of the cases, the conditions for the execution of the test remained without change and correspond to domestic standards for the determination of antiknock values.

In the Federal Republic of Germany (FRG) a single-cylinder BASF installation is being produced, and this installation was developed by the I.G Farben Corporation, with this installation used in a number of European countries for the determination of octane numbers of gasolines in accordance with the motor and research methods.

The BASF is a small-dimension single-cylinder installation which is substantially different from the IT-9 and ASTM-CFR installations in terms of design and dimensions.

The single-cylinder engine in the BASF installation has a variable compression ratio and the following basic technical specifications: the cylinder diameter is 65 mm; the piston stroke, 100 mm; the operating volume of the cylinder, 0.332 liters, i.e., less by a factor of almost 2 than the working volume of the cylinder in the IT-9 and ASTM-CFR installations. At 900 rpm, the engine develops power equal to 1.05 hp.

Depending on the method employed, BASF installations can be used to determine octane numbers under the conditions cited in Table 9.

The method involved in the determination of octane numbers in

TABLE 9

Conditions for Testing Fuels in a BASF Installation

| 1 Показатели | 2 Моторный метод определения октановых чисел | 3 Исследовательский метод определения октановых чисел |
|---|---|---|
| 4 Число оборотов двигателя, *об/мин* . . | 900 | 13 600 |
| 5 Температура топливно-воздушной смеси, °С . . . . . | 165 | Не контролируют |
| 6 Температура всасываемого воздуха, °С | 52 | 52 |
| 7 Температура охлаждающей жидкости, °С . . . . . | 100 | 100 |
| 8 Угол опережения зажигания . . . . . | 10 26° до в. м. т. | |
| | 11 Постоянный для всех степеней сжатия | |
| 9 Аппаратура для замера детонации . . | 12 Детонометр «Филлипс» модель 501А | |

1) Indicators; 2) motor method of determining octane numbers; 3) research method of determining octane numbers; 4) rpm of engine; 5) temperature of fuel-air mixture, °C; 6) temperature of intake air °C; 7) temperature of coolant, °C; 8) crank-angle ignition lag; 9) equipment for measurement of knocking; 10) 26° before top center; 11) constant for all compression ratios; 12) "Phillips" (model 501A) detonometer; 13) not controlled.

BASF installations is basically the same as in the case of IT-9 and ASTM-CFR installations for the corresponding methods. The BASF installation and the test methods in this installation have been standarized in the FRG (standard DIN 51576).

In addition to these installations, the FRG [Federal Republic of Germany] produces a single-cylinder BASF installation with a diesel engine for the determination of cetane numbers of diesel fuels. There is a 4-stroke diesel with a constant compression ratio (of the KD-12 type produced by the MWM Company) in this installation, and this unit has the following basic industrial (technical) specifications: the cylinder diameter is 90 mm; the piston stroke, 120 mm; and the working

volume of the cylinder is 0.85 liters, i.e., somewhat greater than in IT9-3 and ASTM-CFR installations.

The cetane numbers are determined in this installation under the following basic conditions.

| | |
|---|---|
| Engine rpm | 1000 |
| Coolant temperature, °C | 100 |
| Fuel-injection angle, in degrees before top center | 20 |
| Instant of fuel ignition | at top center |
| Quantity of injected fuel, ml/min | 20 |

The installation and method for the determination of the cetane numbers has been standardized in the FRG (standard DIN 51733).

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[List of Transliterated Symbols]

79 ТЭС = TES = TEL = Tetraethyllead

90 О. Ч. = O.Ch. = Oktanovoye chislo = octane number

94 Т = t = toplivo = fuel

94 В = v = vozdukh = air

## Chapter 5

## VAPORIZATION AND MIXTURE FORMATION IN ENGINES

In all types of internal-combustion engines, the onset of fuel combustion is always preceded by complete or partial vaporization of the fuel. In piston-type gasoline engines with spark ignition, the onset of combustion is preceded by practically complete vaporization of the fuel. In piston engines with compression ignition, and in gas-turbine engines, combustion may begin even when only part of the fuel has gone into the vapor state, forming isolated foci of a homogeneous fuel-and-air mixture.

### VAPORIZATION AND MIXTURE FORMATION IN CARBUERETED ENGINES

The quality of mixture formation and the uniformity with which the fuel is distributed among the cylinders of a carbuereted engine are determined to a considerable degree by vaporization of the gasolines used. The fuel economy of a carbuereted engine can be raised sharply by proper selection of the fractional composition of the gasoline, correct and accurate adjustment of the carbueretor, and utilization of external factors. In this connection, it is very important to consider the processes of vaporization and mixture formation in a carbueretor engine and the basic factors influencing these factors.

In carbuereted engines, vaporization of the gasoline and formation of the (working) fuel-and-air mixture have been basically completed by the time the fuel enters the engine's cylinder.

In carbuereted engines, the fuel mixture is distributed among the cylinders in the vaporized state, and for this reason a gasoline of

light fractional composition and high volatility is required for carbuereted engines. It is perfectly obvious that the more completely the gasoline is vaporized before it enters the engine cylinder, the more uniform will be the mixture and the more uniformly will the gasoline be distributed among the engine's cylinders.

Prof. M.M. Maslennikov says that "The degree of evaporation of the fuel before entry into the cylinder that is necessary to produce complete evaporation toward the end of the compression stroke is not exactly known to this day. It may be assumed in approximation that 40 - 50% of the gasoline in a fresh mixture should be vaporized before entry into the cylinder."

However, the danger of incomplete vaporization of the gasoline in the engine's intake system consists primarily in condensation of non-evaporated gasoline drops from the air flow onto the walls of the line, with the result that the mixture has a nonuniform composition, and the liquid film of fuel moving slowly along the walls cannot be distributed uniformly among the cylinders.

Carbueretion Processes

The gasoline escapes from the carbueretor jet in the form of a thin stream whose sectional area is determined by the size of the jet openings.

The equation describing the outflow of the gasoline from the jet is determined to a considerable degree by the shape of the jet itself, which is what governs the laminar or vortical flow of the fuel. In laminar outflow of the gasoline from the jet, this process is described by Poiseuille's law, according to which the head (h), expressed in mm of water column, overcoming the resistance is

$$h = 32\omega \frac{l}{d^2 \eta}.$$

where $\underline{w}$ is the outflow speed of the fuel in m/sec, L is the length of the outflow channel in meters, $\underline{d}$ is the channel diameter in meters, and $\eta$ is the fuel's internal-friction coefficient (viscosity) in $kg \cdot sec/m^2$.

This formula assumes the absence of vorticity in the motion of the fuel flow; this is actually observed only up to a certain critical outflow speed.

In cases of vortical outflow of the gasoline, the equations describing the outflow will depart from Poiseuille's law.

The outflow speed of the gasoline from the jet is determined by the speed at which the air flow moves through the carbueretor diffuser, which, in turn, is determined by the vacuum in the engine's intake system.

The jet of gasoline issuing from the jet immediately enters an air stream moving at a velocity of 70 - 100 m/sec. Under the influence of the aerodynamic pressure of the air and the vortical motion of the outflowing liquid itself, the gasoline jet is broken up into millions of minute droplets. The speed and thoroughness with which the gasoline stream is atomized are determined primarily by the velocity at which the air flow is moving in the diffuser, the outflow speed of the gasoline from the jet, and the physicochemical properties of the gasoline. Surface tension and viscosity are among the most important physical properties of gasoline that influence its atomization.

The gasoline leaves the carbueretor in finely atomized form. Here, part of it vaporizes, withdrawing heat from the air and from the walls of the engine's intake system for evaporation, and the gasoline vapors, entrained by the air flow, enter the engine's cylinder. The unvaporized part of the gasoline may either settle on the walls of the intake manifold or be picked up by the air flow and taken to the cylinder in the form of small droplets.

The quantity of nonvaporized gasoline that will be carried away by the air flow will depend on the extent of atomization and the velocity at which the air is moving. All other conditions the same, the amount of gasoline that will be carried away by the air flow in liquid form will be larger the higher the speed of the air flow and the smaller the atomized gasoline droplets.

The gasoline that has settled in liquid form on the walls of the manifold will also move toward the cylinders, but much more slowly than the air stream. The moving liquid gasoline film is, as a rule, the higher-boiling portion of the gasoline, which evaporates much more slowly.

The air flow in the engine's intake system is not a steady, uniform flow of air, but a continuously vibrating flow. Pulsation and vibration of the air flow arise primarily because of the periodic closing of the engine's cylinder valves. Under certain conditions, the pressure oscillations in the intake system may give rise to instantaneous deposition of gasoline particles from the air in zones of elevated pressure.

To this we should add that the change in direction of the airflow motion as a result of pressure oscillations in the manifold takes place considerably more rapidly than the change in direction of the fine gasoline droplets present in the suspended state, since the inertia of the liquid gasoline particles is greater than that of the gases.

Cessation of the motion of the liquid gasoline particles may result in breakdown of mixture uniformity and nonuniform distribution of the mixture among the cylinders. This phenomenon is particularly marked when multicylinder engines operate on rich mixtures.

Possible consequences of nonuniform distribution of the gasoline among the cylinders are: 1) increased gasoline consumption and lowered economy of the engine and 2) excessively rich or lean mixtures going

individual cylinders; the latter may disturb the smoothness of the combustion process and, in certain cases, even cause overheating of the engine and knocking.

This is why it is necessary that the gasoline be more completely vaporized in the intake systems of carbuereted engines before it enters the cylinder.

Vaporization of Gasoline in Carbueretor Throat

The following three factors exert decisive influence on the completeness with which gasoline is vaporized in the carbueretor throat:

1) the air-flow rate in the carbueretor throat;

2) the temperature of the air entering the throat;

3) the fractional composition of the gasoline.

TABLE 10

Influence of Air-Flow Velocity on Vaporization of Gasolines (air at 30°, $\alpha$ = 1.0)

| 1 Бензин | 2 Температура выкипания, °С | | | | | 5 Испарение в % при скорости воздуха в диффузоре | |
|---|---|---|---|---|---|---|---|
| | 3 н. к. | 10% | 50% | 90% | 4 к. к. | 6 40 м/сек | 6 80 м/сек |
| 7 Авиационный бензин Б-70 | 50 | 80 | 105 | 140 | 179 | 62 | 81 |
| 8 Автомобильный бензин А-66 | 40 | 78 | 142 | 186 | 202 | 46 | 65 |

1) Gasoline; 2) boiling point, °C; 3) initial; 4) final; 5) evaporation in % at diffuser air speed of; 6) m/sec; 7) B-70 aviation gasoline; 8) A-66 automobile gasoline.

In contemporary carbuereted engines, the rate of air flow into the carbueretor diffuser comes to 70 to 100 m/sec, while the rate of air

flow into the carbueretor throat varies from 20 to 40 m/sec.

The velocity of the air flow exerts a considerable influence on the fineness with which the goasoline is atomized and, consequently, on the completeness of its vaporization. All other conditions the same, the gasoline's rate of vaporization will be higher the higher the velocity of the air flow (Table 10).

Thorough atomization of the gasoline increases the total evaporation surface and, consequently, the vaporization rate.

Air temperature is a second important factor which exerts great influence on vaporization of gasoline in the intake system of an engine. This influence is determined by the fact that an increase in air temperature increases the pressure of the gasoline vapors, reduces its surface tension, and accelerates the process of gasoline-vapor diffusion into the air stream.

Influence of Mixture Composition on Vaporization of Gasolines

As a mixture becomes leaner, i.e., as the gasoline-to-air ratio diminishes, evaporation of the gasoline will be intensified, all other conditions the same. This qualitative law remains valid for all air temperatures and flow velocities (Table 11).

Influence of Vapor Pressure of Gasolines on Evaporation

If a gasoline has a high vapor pressure, this means that the grade of gasoline in question contains hydrocarbons possessing high vapor pressures.

However, we may not draw inferences as to the quantative content of light fractions in a gasoline on the basis of vapor pressure alone. A given vapor pressure may be arrived at in a gasoline in either of two different ways. In one case, the gasoline may acquire a high vapor pressure as a result of addition of a small quantity of hydrocarbons possessing high vapor pressures (isopentane) to the gasoline. In another

TABLE 11

Influence of Mixture Composition on Vaporization of Gasolines (air flow in diffuser 80 m/sec, temperature 15°)

| 1 Состав смеси α | 2 Испарение разных бензинов, % | |
|---|---|---|
| | 3 авиационный бензин Б-70 | 4 автомобильный бензин А-66 |
| 0,66 | 60 | 43 |
| 0,80 | 69 | 51 |
| 0,94 | 79 | 58 |
| 1,01 | 84 | 65 |

1) Mixture composition α; 2) vaporization of various gasolines, %; 3) B-70 aviation gasoline; 4) A-66 automobile gasoline.

case, a high vapor pressure may be attained by including in the gasoline a rather large quantity of hydrocarbons possessing medium vapor pressures.

Consequently, the vapor pressure of a gasoline, taken alone with consideration of its fractional composition, is not an adequate index to its vaporizability. Let us illustrate this using an example. There are two grades of gasoline with the same saturation vapor pressure (340 mm Hg) but different fractional compositions.

In the first gasoline (A-66) we have a considerable quantity of the butane-pentane fraction. In the second gasoline (B-70), this fraction is totally absent. For the second gasoline to have the same vapor pressure as the first, it must contain a considerable quantity of hydrocarbons with medium vapor pressures, as is reflected by its fractional composition. On vaporization in a stream of air, the second gasoline will, all other conditions the same, vaporize faster, although its starting properties at low temperatures will be better than those of the first gasoline. This effect is also observed on comparison of the vaporizabilities of aviation and automobile gasolines.

For a given vapor pressure, a gasoline with a lighter fractional composition vaporizes much more completely and rapidly in the air stream (Table 12).

But if the gasolines have the same fractional composition, the vapor pressure may, in this case, serve as an index to its vaporizability. The higher the vapor pressure of a gasoline, the better will it

TABLE 12

Vaporization of Gasolines in Air Flow on Carbueretion (air flow in diffuser 80 m/sec, $\alpha = 1.0$)

| 1 Бензин | 2 Давление паров при 38°, мм рт. ст. | 3 Испарение бензина в % при температуре воздуха | |
|---|---|---|---|
| | | 20° | 50° |
| 4 Авиационный бензин Б-70 | 340 | 56 | 74 |
| 5 Автомобильный бензин А-66 | 346 | 48 | 62 |

1) Gasoline; 2) vapor pressure at 38°, mm Hg; 3) vaporization of gasoline in % at air temperature of; 4) B-70 aviation gasoline; 5) A-66 automobile gasoline.

TABLE 13

Influence of Fractional Composition of Gasoline on its Vaporization during Carbueretion

| 1 Бензин | 2 Температура выкипания, °С | | | | | 5 Испарение бензина в % при $\alpha$=1,0 и температуре воздуха +15° |
|---|---|---|---|---|---|---|
| | 3 н. к. | 10% | 50% | 90% | 4 к. к. (98%) | |
| 6 Авиационный бензин Б-70 | 50 | 80 | 105 | 140 | 170 | 50 |
| 7 Автомобильный бензин А-66 | 40 | 78 | 142 | 186 | 202 | 45 |

1) Gasoline; 2) boiling point, °C; 3) initial; 4) final; 5) vaporization of gasoline in % for $\alpha = 1.0$ and air temperature of +15 degrees; 6) B-70 aviation gasoline; 7) A-66 automobile gasoline.

vaporize.

As we know, however, the saturation vapor pressure of any liquid, including gasolines, is a function of temperature: the higher the temperature, the higher the vapor pressure. Consequently, we may increase not only the vapor pressure of a gasoline by raising the temperature, but its vaporizability as well.

The sharp increase in vaporizability of gasoline that takes pla

when the temperature of the air entering the carbueretor is raised results in preheating of the gasoline droplets, and this increases the vapor pressure and improves vaporization.

Influence of Fractional Composition of Gasolines

The fractional composition of a gasoline has a strong influence on its evaporation during carbueretion. All other conditions the same, the lighter the fractional composition, the greater will be the portion of the gasoline that enters the vapor state in the throat prior to entering the engine's cylinders. This relationship is clearly evident from Table 13.

VAPORIZATION AND MIXTURE FORMATION IN INJECTED ENGINES

In fuel-injection engines, the gasoline is fed into the cylinder through a nozzle during the intake stroke. The time during which the gasoline vaporizes in the engine cylinder is determined by the time elapsing from the start of injection to ignition of the mixture by the electric spark during the compression stroke. The duration of this period depends on the engine rpm's, on the injection angle, and on the spark-advance angle, but amounts to only hundredths of a second.

Thus, for example, the gasoline for the ASh-82FH engine is injected into the cylinder during the intake stroke with a $30^{\circ}$ delay after TDC, and ignition is set $20^{\circ}$ before TDC in the compression stroke; the vaporization time of the gasoline in the cylinder is $360 - 50 = 310^{\circ}$ of crankshaft revolution or, converted, 0.02 to 0.03 sec. Consequently, only 0.02 sec is set aside for the entire process of gasoline vaporization and for priming of the mixture for ignition at n = 2500 rpm.

In accordance with the manner and conditions of gasoline vaporization in the cylinder, the total vaporization time may arbitrarily be broken down into two parts:

a) vaporization of the gasoline during the intake stroke at a con-

stant pressure that is actually very close to atmospheric; during this period, the air entering through the intake valve sets up vigorous turbulent motion inside the cylinder, and this improves mixing of the gasoline with the air and residual gases and speeds up vaporization of the gasoline;

b) vaporization of the gasoline during the compression stroke, when the vortical motions of the mixture slow down to some extent and the pressure and temperature inside the cylinder rise rapidly.

Vaporization in Intake Stroke

In an injection-type engine, the gasoline is fed into the cylinder through a special nozzle in a finely atomized state; simultaneously with the gasoline, air enters through the intake valve at a speed of about 80 m/sec.

At a certain point in time, therefore, a spray of gasoline consisting of minute droplets from 1 to 5 $\mu$ in diameter is being acted upon by two air flows which, being directed onto the surface of the spray at different angles, give rise to a chaotic vortical motion relative to the surface of the gasoline droplet. It is this vortical motion of the air in the engine cylinder that produces the extremely high rate of evaporation of gasoline in the engine's cylinder.

For the intake stroke, the pressure in the cylinder may be regarded as equal to atmospheric.

The high speeds of the vortical motion of the air and the low pressure inside the cylinder are the favorable factors that insure a high rate of gasoline vaporization in the engine cylinder during the intake stroke.

Vaporization During Compression Stroke

In certain cases, vaporization of the gasoline in the cylinder has not been completed at the end of the intake stroke, but continues

into the compression stroke.

The conditions for vaporization of the gasoline in the compression stroke differ considerably from those prevailing during the intake stroke. The fundamental differences in the gasoline-vaporization conditions in the compression stroke are as follows:

a) the vortical motions of the air slow down during the compression stroke, but the air continues to move as a result of the piston's motion; the speed of this motion is about 10 to 11 m/sec;

b) the pressure inside the cylinder rises sharply, reaching 15 to 20 atmospheres, depending on compression ratio and supercharging;

c) the temperature of the air (mixture) rises sharply and may reach 400 to 550° by the time the mixture is ignited.

Consequently, vaporization of gasoline in the cylinder during the compression stroke is somewhat retarded by the increased pressure and accelerated considerably by the sharp increase in air temperature.

In view of the relatively light fractional composition of gasolines, we may assume that the influence of high air temperature on vaporization of the fuel is considerably greater than the retarding effect of the elevated pressure in the cylinder during the compression stroke.

Influence of Air Temperature on Vaporization

The speed and completeness of vaporization of the gasoline injected into the engine cylinder is determined to a considerable degree by the temperature of the air entering the cylinder.

Depending on the temperature of the outside air and supercharging pressure, the air may be heated to 50 to 100° even in the engine's supercharger. On entering the cylinder, the air is further heated as a result of contact with the hot surfaces, as well as by mixing of the fresh air with the residual gases inside the cylinder. During the in-

duction process (intake stroke), the temperature of the air is raised by 50 to 100°; by the beginning of the compression stroke, the mixture temperature has reached 100 to 200°. In engines with compression ratios from 6.0 to 7.0, the mixture temperature reaches 400 to 550° and the pressure 15 atmospheres by the end of compression.

TABLE 14

Influence of Temperature Conditions in Engine on Vaporization of Gasoline

| 1 Бензин | 2 Температура стенок камеры и цилиндра, °С | 3 Испарение топлива в цилиндре (в %) при | | | |
|---|---|---|---|---|---|
| | | α=0,7 | | α=1,0 | |
| | | 4 Температура воздуха, °С | | | |
| | | 25° | 50° | 25° | 50° |
| 5 Авиационный бензин Б-100/130 . . | 20 | 61 | 79 | 71 | 88 |
| | 50 | 97 | 99,7 | 100 | 100 |
| 6 Автомобильный бензин А-66 . . . . | 20 | 43 | 55 | 46 | 64 |
| | 50 | 60 | 70 | 66 | 77 |

1) Gasoline; 2) temperature of chamber and cylinder walls °C; 3) vaporization of fuel in cylinder (in %) at; 4) air temperature, °C; 5) B-100/130 aviation gasoline; 6) A-66 automobile gasoline.

Research has shown that for a given quality of gasoline, the speed and completeness of its evaporation in the engine cylinder are determined in the final analysis by the temperature conditions under which the motor is operating.

For each grade of gasoline, there exists a certain minimum temperature at which the gasoline will be completely vaporized in the engine chamber, depending on its fractional composition. This minimum temperature necessary for vaporization of the gasoline is determined by the temperature state of the engine and the temperature of the air entering the cylinders.

Gasolines of light fractional composition vaporize practically instantly on injection into an operating, warmed-up engine and go over

into the gaseous state.

As the fractional composition of the gasoline becomes heavier (for a given set of engine temperature conditions), vaporization of the gasoline deteriorates. This phenomenon is clearly illustrated by the data of Table 14.

In examining Table 14, it should be taken into account that these data were obtained under engine-operating conditions in which high turbulence of the air is observed in the engine cylinder. Consequently, these data cannot be extended to the time at which the engine is started, when the cylinder-wall temperature may have been brought up to the necessary level, but motion (turbulence) of the air is almost totally absent. On starting, vaporization of the gasoline injected into the cylinder approaches the conditions of static evaporation of a stream of gasoline in quiet air.

Influence of Velocity of Air Motion on Vaporization

Until recently, investigators regarded air turbulence in the engine cylinder as a factor that exerted a strong influence on the rate of propagation of the flame front, without having any link to the process of gasoline vaporization.

However, intensification of the air's turbulent motion in the cylinder gives rise to an increase in the rate of flame-front propagation, not only due to mechanical agitation of the burning mixture layer, but also as a result of the more complete vaporization of the gasoline and the more uniform distribution of the fuel throughout the volume of the air.

The speed at which the piston is travelling is determined by the number of engine rpm's and the length of its stroke, and may be computed by the following formula:

$$w = \frac{sn}{30},$$

where w is the speed of the piston in m/sec, s is the length of the piston stroke in meters, and n is the number of engine rpm's.

For an engine with a piston stroke of 170 mm operating at 2000 rpm's the piston speed is

$$w = \frac{sn}{30} = \frac{0.17 \cdot 2000}{30} = 11 \text{ m/sec}$$

Experimental researches confirm that the rate of displacement of the air in the cylinder is about 12 m/sec when air is entering the cylinder at a rate of 80 m/sec.

Experimental studies have shown that the intensity of air turbulence in the cylinder exerts enormous influence on the speed and completeness of vaporization of the gasoline injected into the cylinder.

As a rule, all other conditions the same, vaporization is better the higher the turbulence of the air.

The strong influence that turbulence exerts on gasoline vaporization is due to the following factors:

a) the high velocity at which the air is moving breaks up the stream more thoroughly and reduces the size of the gasoline droplets, thereby increasing the vaporization surface;

b) the high speed at which the air is moving accelerates vaporization of the gasoline drops because the air draws vapor from the drop surfaces and carries the vapor away from the immediate vicinity of the drops;

c) turbulence considerably improves the exchange of heat between the various layers of air and, consequently, intensifies heating of the gasoline droplets suspended in the air;

d) in turbulence, i.e., when we observe a high speed of mass transfer relative to the evaporating droplet surface, the process in which gasoline vapors diffuse into the air increases sharply.

The influence of intensity of air motion on gasoline vaporization is shown below.

| 1 Скорость поступления воздуха в цилиндр, м/сек | 2 Испарение бензина (в %) при температуре цилиндра 50° и воздуха 20°С | |
|---|---|---|
| | $\alpha=0,7$ | $\alpha=1,0$ |
| 30 | 60 | 66 |
| 45 | 71 | 78 |
| 60 | 75 | 82 |

1) Rate of entry of air into cylinder, m/sec; 2) vaporization of gasline (in %) at cylinder temperature of 50° and air temperature of 20° C.

## Influence of Temperature State of Engine on Vaporization of Gasoline

TABLE 15

Cylinder-Wall Temperature at which Fuel is Fully Vaporized

| 1 Топливо | 2 Температура выкипания, °С | | | | | Температура стенок цилиндра и камеры сгорания 3 (в °С) при | |
|---|---|---|---|---|---|---|---|
| | 4 н. к. | 10% | 50% | 90% | 5 к. к. | $\alpha=0,7$ | $\alpha=1,0$ |
| 6 Авиационный бензин Б-70 | 50 | 80 | 105 | 140 | 179 | 72 | 65 |
| 7 Автомобильный бензин А-66 | 40 | 78 | 142 | 186 | 202 | 110 | 100 |
| 8 Лигроин тракторный | 93 | 108 | 142 | 212 | 237 | 135 | 120 |
| 9 Керосин | 138 | 161 | 202 | 242 | 275 | 180 | 170 |

1) Fuel; 2) boiling temperature, °C; 3) cylinder-wall and combustion-chamber temperature (in °C) at; 4) initial; 5) final; 6) B-70 aviation gasoline; 7) A-66 automobile gasoline; 8) tractor ligroin; 9) kerosene.

The speed with which an aviation engine can be prepared for take-off and its normal operation usually involve attainment of a certain temperature regime in the engine.

The thermal state of the engine is ordinarily judged from the temperature of the coolant and the oil temperature in the system and at the outlet, etc.

Bringing the engine up to a certain temperature is dictated by the necessity of ensuring complete vaporization of the gasoline in the cylinder by the time the mixture is ignited.

The minimum temperature necessary in the engine's combustion chamber will be different for gasolines with different fractional compositions. The heavier the fractional composition of the gasoline, the higher will be the temperature inside the cylinder at which it vaporizes completely. This statement is clearly illustrated by Table 15, which shows the minimum cylinder-wall and combustion-chamber temperatures necessary for complete vaporization of fuels having various fractional compositions.

The figures in this table indicate that under normal conditions, gasoline is completely vaporized in an aviation engine if the cylinder and combustion-chamber walls are no cooler than 72°.

In operation on automobile gasoline, this temperature may not fall lower than 110°.

Consequently, there is every justification for assuming that practically all of the gasoline is in the vapor state in a warmed-up aviation engine by the time the mixture is ignited.

## VAPORIZATION AND MIXTURE FORMATION IN COMPRESSION-IGNITION ENGINES (DIESELS)

In compression-ignition engines, the mixing and combustion processes are superimposed on one another. Very little time is allowed for mixing processes and for preparation of the fuel for combustion in these engines. As a result, uniform distribution of the fuel in the air volume is an exceptionally important factor. Distribution of the fuel droplets over the entire combustion-chamber volume is achieved by fine atomization of the fuel and by giving the spray a certain shape and range.

In the initial stage of mixing, isolated zones at which fuel vapors have accumulated form in the volume of the compressed air. As the fuel drops evaporate, and under the influence of turbulence, the isolated zones of fuel vapor expand to form more or less large volumes filled with fuel vapors.

For given fuel characteristics, the completeness of vaporization of the atomized-fuel droplets and mixture formation are determined by the fineness and uniformity of the spray, proper selection of the shape and size of the cone, the ambient temperature and the time provided for these processes. The chemical composition of the fuel exerts virtually no influence on the mixing process.

It is assumed that due to the extremely limited time available for priming of the mixture in compression-ignition engines, the vaporization process of the fuel is not completed by the time it is ignited. This is one of the basic reasons why combustion in a diesel begins with almost simultaneous ignition of the mixture at different points. The nature of the combustion-process development in this case will be determined chiefly by chemical (oxidation) reactions.

Fineness of Atomization

The fineness of atomization is determined by the average droplet size in the spray cone. Atomization is regarded as fine if the average fuel-droplet diameter is relatively small and as coarse if the average droplet diameter is large.

Prof. T.M. Mel'kumov takes the position that the average droplet diameter of the atomized fuel is 2 to 5 $\mu$ for high-speed diesels. Given such a droplet diameter, the dose of fuel injected into the cylinder is broken up into several million drops.

When the injection pressure is raised, the average droplet diameter diminishes and, consequently, the fineness of fuel atomization

increases, as will be seen from the following data.

| 1 Давление впрыска, *ат* | 50 | 100 | 150 | 200 | 250 | 300 |
|---|---|---|---|---|---|---|
| 2 Средний диаметр капель топлива, *мк* | 40,00 | 33,75 | 26,75 | 20,00 | 13,75 | 4,37 |

1) Injection pressure, atmospheres; 2) average fuel-droplet diameter, μ.

The data above indicate that as the injection pressure is increased by a factor of 6, the average fuel-droplet diameter is reduced by a factor of 9.

With increasing density of the medium into which the fuel is injected, the fineness of atomization increases. However, Prof. T.M. Mel'kumov has advanced the hypothesis that this qualitative relationship can obviously be correct only up to a certain limit, above which the reverse effect may occur, i.e., an excessive increase in back pressure will slow the motion of the stream considerably and interfere with its decomposition into fine droplets.

These conclusions are also confirmed by experimental research. Thus, for example, on injection of fuel into a cylinder at atmospheric pressure, the average droplet diameter is 23 μ; at a cylinder pressure of 5 atmospheres, the average droplet diameter is 17 μ and at a 10-atmosphere cylinder p essure the average droplet diameter is 13 μ.

Thus, an increase in injection pressure by a factor of 2 causes a reduction of approximately 20% in average fuel-droplet diameter.

The viscosity and surface tension of the fuel exert considerable influence on its atomization. The higher the viscosity and surface tension, the poorer the atomization, i.e., the larger the average diameter of the atomized-fuel droplet.

MIXTURE FORMATION IN GAS-TURBINE ENGINES

In piston engines with spark ignition, combustion is determine

a considerable degree by the chemical composition of the fuel.

In gas-turbine engines, combustion is chiefly a function of the physical characteristics of the fuel. For this reason, mixing and the characteristics of the fuel, which influence mixing, will determine the combustion process to a considerable degree in gas-turbine engines.

In examining the processes of mixing and combustion, we may arbitrarily break the gas-turbine engine's combustion chamber up into three zones: 1) a mixing zone, 2) the combustion-zone proper, and 3) a zone of final combustion and dilution of the gases with secondary air.

Under real conditions, these zones do not have sharp boundaries and one merges into the other progressively with overlapping.

It has been established by research that the proficiency of the mixing process is determined primarily by the fineness of atomization, the vaporizability of the fuel, and the intensity of air turbulence.

Injection and Atomization of Fuel

Injection and atomization of the fuel in the combustion chamber of the gas-turbine engine represent the initial stage in the cycle, and one that determines to a considerable degree the course of its subsequent stages.

The quality of fuel atomization is evaluated by the fineness and uniformity as well as the range of the injected jet.

The fineness of atomization is characterized by the average diameter of the atomized-fuel droplets; the narrower the range into which the droplet diameters fall, the more uniform is the atomization. The more uniformly the fuel is atomized in the volume of the air flow passing through the combustion chamber, the more complete will mixing become.

Vaporization of Fuel

The droplets of atomized fuel, which are in the suspended state,

evaporate and move in the direction of the combustion zone. The vaporization process of finely atomized fuel droplets moving at a certain velocity relative to the medium surrounding them is extremely complex.

When a fuel droplet is washed by a stream of air, the flow breaks away at its surface, and a dead zone forms behind the drop. As a result, vaporization takes place at different rates from various zones on the drop surface. In this case, the rate of vaporization is determined not only by temperature, the pressure of the medium, the vapor pressure of the evaporated fuel and droplet size, but also by the hydrodynamic conditions of the process, i.e., by the speed of the relative motion of the gas flow and its turbulence.

As the drop moves in the flow, the temperature of the surface and the liquid nucleus of the droplet rise steadily as a result of heat transfer from the combustion zone. It is assumed that when the temperature of a fuel droplet has reached the liquid's boiling point, the saturation vapor pressure at the droplet surface is higher than the prevailing pressure. Under such conditions, the rate of diffusion of fuel vapor into the surrounding medium (air) becomes very large. In this case, the rate of droplet evaporation in the gas flow is determined chiefly by the flow of heat from the surrounding medium to the droplet surface. A theoretical and experimental investigation of the heat-transfer processes and the rate of heating of droplets in a gas stream has been made by Prof. D.N. Vyrubov.

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## Chapter 6

## COMBUSTION OF FUELS IN ENGINES

Internal-combustion engines are heat machines intended for the conversion of the chemical energy of a fuel into mechanical energy. Chemical energy is converted into mechanical energy by burning a fuel in the combustion chamber of an engine and using the work of the expanding gaseous products of fuel combustion.

On the basis of the technical principles involved in the derivation of mechanical energy, thermal engines can be divided into piston, turbine, and jet engines. On the basis of the combustion process, we distinguish continuous-combustion and periodic-combustion engines; on the basis of the fuel-ignition method employed, we distinguish auto-ignition and forced-ignition engines.

Generally, gasoline, kerosene, solar, and heavier fractions of petroleum are used as the fuel in internal-combustion engines.

The combustion of a fuel is a fast chemical reaction involving the oxidation of the fuels with oxygen, and this reaction is accompanied with the liberation of heat and the appearance of a flame. The process of fuel combustion in engines lasts for thousandths of a second. In order for the fuel entering the combustion chamber of the engine to be completely burned up during such a short interval of time, the fuel is subjected to preliminary preparation involving its atomization, vaporization, and the mixing of the fuel vapors with an oxidizer.

The chemical preparation of the mixture takes place simultaneously and involves the initial preflame reactions between the fuel molecule

and the oxidizer. The extent of the chemical preparation of the fuel-oxidizer mixture is determined by the temperature and the pressure of the mixture.

Generally the oxygen of the air is used as the fuel oxidizer in engines. Only in certain types of engines, in particular in liquid fuel rocket engines, are special chemical compounds (nitric acid, liquid oxygen, etc.) used as oxidizers.

In order for the chemical reaction of combustion to begin in the prepared fuel-air mixture, an initial flame focus must be created within the mixture, and the flame must propagate from this focus throughout the entire mixture until complete (total) combustion is achieved. In engines, the initial flame focus (the ignition of the mixture) is generally accomplished by means of an electric spark (forced-ignition engines). Another ignition method is possible, and here the entire volume of the fuel-air mixture is heated to a temperature at which the initial flame foci appear spontaneously (without forced ignition) within the mixture (autoignition engines - diesels).

The propagation of the flame from the initial foci takes place as a result of the heating of a thin layer of fresh mixture in contact with the surface of the flame focus, and this layer is heated to a temperature in excess of the ignition temperature. The ignition of a fresh mixture is enhanced by active particles - atoms, radicals, and ions - diffusing into the fresh mixture from the igniting mixture. The thin layer of gas in which the combustion reaction takes place is referred to as the flame front.

In order for the flame to begin its propagation through the mixture the following conditions must be maintained. First of all, the energy of the initial flame focus (the power of the spark) must be sufficiently high. Given inadequate spark power, the heat liberated in

TABLE 16

Concentration Limits for Propagation of Flame for Mixtures of Fuels (Combustibles with Air [1, 2]

| 1 Горючее | 2 Граница зажигания в % горючего по объему | | Горючее | Граница зажигания в % горючего по объему | |
|---|---|---|---|---|---|
| | 3 нижняя | 4 верхняя | | нижняя | верхняя |
| 5 Водород | 4,0 | 75,0 | 17. Гептан | 1,2 | 6,7 |
| 6 Окись углерода | 12,5 | 74,0 | 18. Толуол | 1,4 | 6,8 |
| 7 Ацетилен | 2,5 | 80,0 | 19. Изооктан | 1,1 | — |
| 8 Метан | 5,3 | 14,0 | 20. Ацетон | 3,0 | 11,0 |
| 9 Этан | 3,0 | 12,5 | 21. Метиловый спирт | 6,7 | 36,5 |
| 10 Пропан | 2,2 | 9,5 | 22. Этиловый спирт | 3,3 | 19,0 |
| 11 Бутан | 1,9 | 8,5 | 23. Этиловый эфир | 1,9 | 48,0 |
| 12 Бутилен | 2,0 | 9,6 | 24. Окись этилена | 3,0 | 80,0 |
| 13 Пентан | 1,5 | 7,8 | 25. Диэтил-перекись | 2,3 | — |
| 14 Гексан | 1,2 | 7,5 | 26. Метиламин | 4,9 | 20,7 |
| 15 Циклогексан | 1,3 | 8,0 | 27. Диметиламин | 2,8 | 14,4 |
| 16 Бензол | 1,4 | 7,1 | 28. Триметиламин | 2,0 | 11,6 |

1) Fuel (combustible); 2) ignition limit, in % of fuel (combustible) by volume; 3) lower; 4) upper; 5) hydrogen; 6) carbon monoxide; 7) acetylene; 8) methane; 9) ethane; 10) propane; 11) butane; 12) butylene; 13) pentane; 14) hexane; 15) cyclohexane; 16) benzene; 17) heptane; 18) toluene; 19) isooctane; 20) acetone; 21) methyl alcohol; 22) ethyl alcohol; 23) ethyl ether; 24) ethylene oxide; 25) diethyl peroxide; 26) methylamine; 27) dimethylamine; 28) trimethylamine.

the initial flame focus is dispersed throughout the volume of the fresh mixture and there is no flame propagation. Secondly, the content of fuel in the mixture must lie within a definite range, beneath and above which flame propagation will not take place regardless of the power of the ignition spark. We distinguish an upper ignition limit which is obtained with the highest fuel (combustible) content in the mixture, and a lower limit which occurs in the case of least fuel (combustible) content in the mixture. Table 16 presents the values of concentration ignition limits (limits of flame propagation) for mixtures of certain fuels (combustibles) with air.

Consequently, the process of fuel combustion in engines can be presented as consisting of several individual processes: the physical

chemical preparation of the fuel-air mixture, the formation of the initial flame foci (ignition of the mixture), and the propagation of the flame from the initial foci through the fresh mixture.

Depending on the manner in which the initial flame foci were formed within the mixture (forced ignition or autoignition), the subsequent propagation of the flame from these foci takes place in a variety of ways. In the case of autoignition, when the mixture is heated to a sufficiently high temperature and is chemically well prepared, the flame is propagated at a substantially higher rate than in the case of the ignition of a cold mixture by a spark.

In view of the turbulent motion of the fuel-air mixture in engines, individual portions (volumes) of the fresh mixture may enter an area behind the flame front, into the products of combustion heated to high temperatures. Therefore in forced-ignition engines some portion of the fuel is subjected to combustion as a result of autoignition. At the same time, in autoignition engines a substantial portion of the fuel injected into the cylinder, subsequent to which ignition took place, is burned up as a result of the propagation of the flame through a comparatively cold and chemically poorly prepared mixture.

Consequently, in each type of internal-combustion engine a portion of the mixture is subjected to combustion at a high rate as a result of autoignition and the remaining portion – at a slower rate – as a result of the propagation of the flame through a "cold" and chemically poorly prepared mixture.

The greater the fraction of the mixture consumed as a result of autoignition, the greater the quantity of heat released per unit time into the combustion chamber of the engine, and the greater, all other conditions being equal, the efficiency of the engine. This method of increasing engine efficiency has a number of limitations associated

with the disruption of the normal combustion process when the above-determined limits of the portion of fuel consumed as a result of autoignition are increased. In the majority of cases, these limitations are associated with the features encountered in the preflame chemical reactions in hydrocarbon-air mixtures.

## PREFLAME REACTIONS IN THE CASE OF THE AUTOIGNITION OF HYDROCARBON-AIR MIXTURES

In hydrocarbon-air (or oxygen) mixtures heated to temperatures in excess of the autoignition temperature, the appearance of flame foci is preceded by preflame chemical reactions. The preflame reactions involving the interaction of molecules from the fuel (combustible) and oxidizer become possible at a mixture temperature substantially lower than the autoignition temperature. These chemical reactions are exothermic, i.e., they take place with liberation of heat. In this case, the temperature of the reacting mixture increases, and this in turn results in an increase in the rate of the preflame reactions. If the quantity of heat removed from the reacting mixture is less than that liberated during the reaction, after a certain interval of time (ignition lag) the mixture will heat up to a temperature in excess of the autoignition temperature and an explosion will occur.

Figure 33 shows the autoignition limits for hydrocarbon-air mixtures as a function of pressure and mixture temperature. The region in which the mixture ignites can be divided into three zones – a low-temperature, a transition, and a high-temperature zone.

The preflame oxidation reactions are chain reactions with degenerate branching of the chains, i.e., reactions in which the branching of the chains is governed by stable intermediate products – peroxides and aldehydes – which decay substantially more easily than the initial substances and form three radicals – active centers of reaction. The

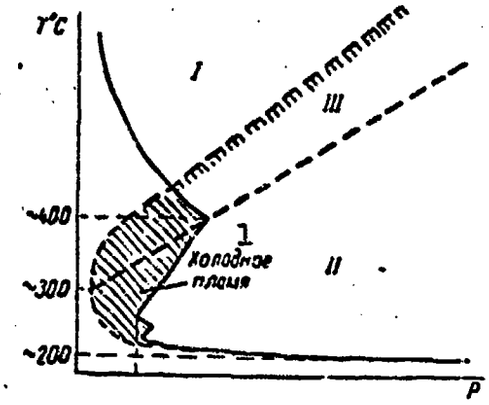


Fig. 33. Typical diagram of autoignition zones for hydrocarbons. I) Zone of high-temperature single-stage ignition; II) zone of low-temperature multistage ignition; III) transition zone; 1) cold flame.

above-enumerated ignition zones differ from one another in terms of the nature of the reactions which result in the degenerate branching of the chains. The initiation of the chain reaction in the gas mixture can be represented by the following equations:

$$RH+O_2 \rightarrow R^{\cdot}+HO_2^{\cdot},$$

$$R^{\cdot}+O_2 \rightarrow ROO^{\cdot}$$

(peroxide radical).

The subsequent development of a chain reaction in each of the autoignition zones is shown in Table 17.

The substances responsible for the branching of the chains in the low-temperature and high-temperature zones are, respectively, the peroxides and the aldehydes. In order to branch the chains through the peroxides a small energy of activation is required; therefore, the branching may take place at relatively low temperatures. In the case of high temperatures the peroxide radical decays and a branching reaction through the aldehydes becomes possible, and for this reaction to take place a higher activation energy is required than for the branching through the peroxides.

In the transition zone, the chains become branched primarily as a result of the interaction of the peroxide radicals with the aldehydes, i.e., the interaction of those substances which result in the branching of the chains in the low-temperature and high-temperature zones.

In view of this, periodic self-oscillatory chemical reactions may take place in the transition zone.

In References [3, 4] D.A. Frank-Kamenetskiy developed the theory

TABLE 17

Basic Reactions in the Development of Chains in Various Autoignition Zones

| 1 Зона самовоспламенения | 2 Основные реакции | |
|---|---|---|
| | 3 продолжение цепи | 4 вырожденное разветвление |
| 5 Низкотемпературная | $ROO\dot{}+RH \rightarrow ROOH+\dot{R}$ | $ROOH \rightarrow R\dot{O}+\dot{O}H$ |
| 6 Переходная | $ROO\dot{} \rightarrow R'CH \rightarrow R'CHO+\dot{O}H$ (O–OH) $\dot{O}H+RH \rightarrow \dot{R}+H_2O$ | $ROO+R'CHO \rightarrow R\dot{O}+\dot{O}H+R'C\dot{O}$ |
| 7 Высокотемпературная | $R'\dot{O} \rightarrow R''CH_2O \rightarrow CH_2O+\dot{R}''$ $R'C\dot{O}+RH \rightarrow R'CHO+\dot{R}$ $ROO\dot{} \rightarrow R'\dot{O}+R''CHO$ | $R'CHO+O_2 \rightarrow R'C\dot{O}+H\dot{O}_2$ $CH_2O+O_2 \rightarrow HC\dot{O}+H\dot{O}_2$ |

1) Autoignition zone; 2) basic reactions; 3) continuation of chain; 4) degenerate branching; 5) low-temperature; 6) transition; 7) high-temperature.

of the occurrence of self-oscillatory chemical reactions in the oxidation of hydrocarbons. Subsequently, Yu.G. Gervart and D.A. Frank-Kamenetskiy set up experiments in which they observed the periodic occurrence of cold flames in a fuel-air mixture [5].

A feature of the transition zone, closely associated with the phenomenon of periodic preflame reactions, is the anomalous change in the autoignition lag: with a rise in temperature the autoignition lag does not diminish, but rather increases. These features encountered in the preflame reactions in the transition zone are of great practical significance.

If the cold fuel-air mixture enters a zone of relatively high temperatures, as the mixture heats up preflame reactions will take place within the mixture and these will initially correspond to a low-temperature zone, then to the transition zone, and finally to the high-temperature zone. In these cases, we find the phenomenon of multistage

ignition. Several flashes of a light-blue flame (the so-called "cold" flame) appear in a fuel-air mixture during the autoignition lag and correspondingly there are a number of pressure jumps.

After a number of such flashes the mixture ignites. The intervals between the pressure jumps or flashes of cold flame characterize the duration of each stage of the multistage autoignition process. There is reason to expect that the appearance of these cold flames will take place each and every time there is a change in the nature of the reactions determining the degenerate branching of the chains (for example, with a change in the temperature of the mixture and the transitions of the mixture from one ignition zone to another).

The nature of the preflame reactions taking place within the mixture is also a function of the phase state in which the fuel enters the high-temperature zone. If the fuel enters the high-temperature zone in the liquid phase, in the form of drops, yet another stage in the multistage autoignition process is possible, i.e., the liquid-phase stage of fuel oxidation.

## THE EFFECT OF LIQUID-PHASE OXIDATION OF A VAPORIZED FUEL ON THE COURSE OF PREFLAME REACTIONS IN ENGINES

The oxidation of hydrocarbons in the liquid phase may take place at substantially lower temperatures than in the case of vapor phase. We can expect that in engines drops of atomized cold fuel will be subject to sufficiently intense liquid-phase oxidation to the point at which they vaporize. This liquid-phase oxidation may have a substantial effect on the course of the subsequent preflame reactions in the vaporizing fuel. To this time no experimental verification of the possibility of liquid-phase oxidation of drops of atomized fuel in engines has been undertaken. We set up the following experiments which confirmed the possibility of the liquid-phase oxidation of fuel drops in engines.

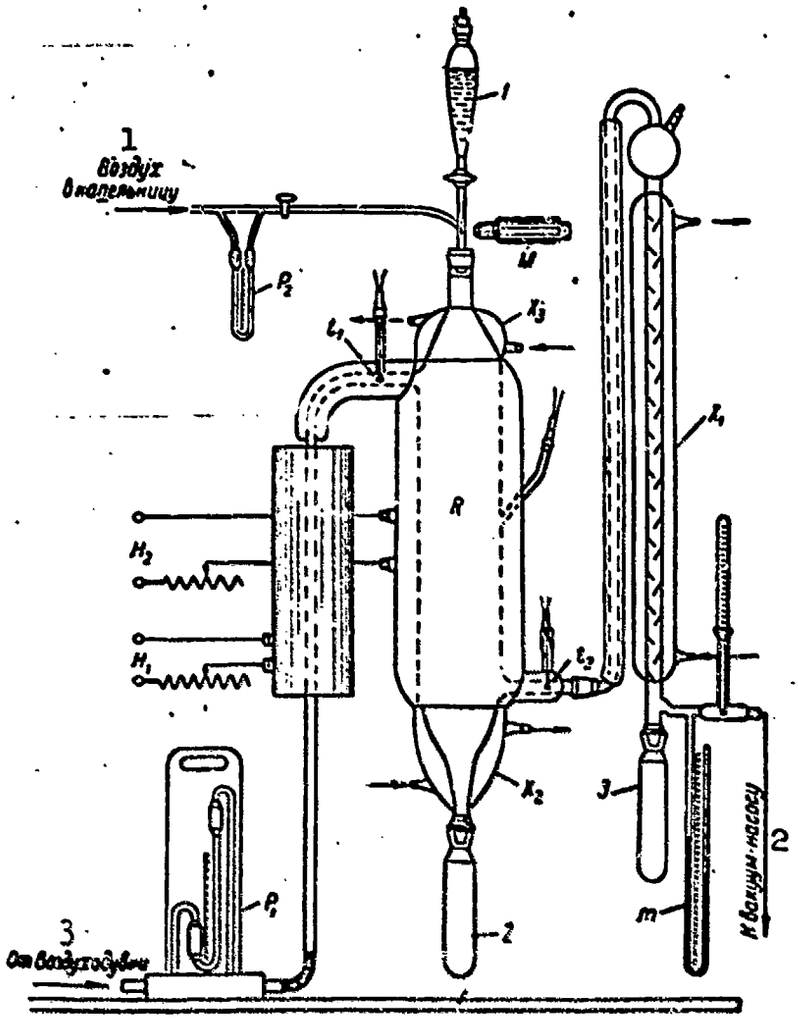


Fig. 34. Installation for investigation of oxidizability of fuel drops. 1) Air to dropper; 2) to vacuum pump; 3) from air blower.

The investigation was carried out on a laboratory installation of which we present a diagram in Fig. 34. The installation consisted of a fuel tank 1 with a dropper, thus making it possible to produce drops of desired dimensions; a reactor R in which the given temperature, pressure, and rate of air flow was maintained; receivers for the liquid 2 and condensing vapor 3 fuel phases. The vaporized portion is condensed in the cooler $Kh_1$.

The coolers $Kh_2$ and $Kh_3$ restricted the dimensions of the reaction zone. The air which entered the reactor was heated by furnace $H_1$. To

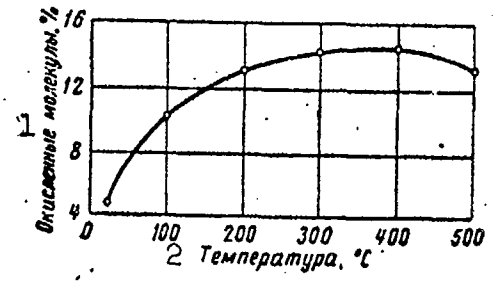


Fig. 35. Effect of temperature on oxidizability of fuel drops (drop diameter, 1.0 mm). 1) Oxidized molecules, %; 2) temperature, °C.

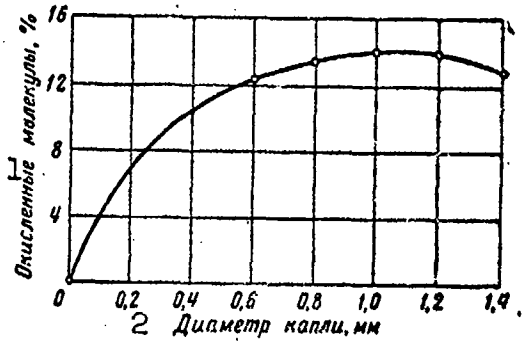


Fig. 36. Effect of drop dimension on the oxidizability at an air temperature of 300°. 1) Oxidized molecules, %; 2) drop diameter, mm.

compensate for the heat losses in the reactor, the latter was equipped with an electric heater which maintained the air temperature ($t_2$) at the outlet from the reactor equal to the air temperature ($t_1$) at the inlet to the reactor. The air flow rate was determined by means of rheometers $R_1$ and $R_2$, and the air pressure was determined by means of manometer m. The dimensions of the drops are estimated by means of a counting microscope M. A judgment was arrived at with respect to the degree of oxidation of the drops and fuel vapors collected in receivers 2 and 3 by the direct determination of the oxygen content through a microscope. The obtained results were expressed in the form of a conditional percentage of the oxidized molecules. If we assume, for example, that each molecule of diesel fuel with a molecular weight of 178 is bound to 1 atom of oxygen, the oxygen content in % by weight in the oxidized fuel amounts to (16 x 100) / 178 + 16) = 8.25%. This quantity corresponds to 100% of the oxidized molecules. If the oxygen content a in the fuel is expressed in % by weight, the percentage of oxidized molecules will be:

$$M_0 = \frac{100}{8,25} a = 12,13a.$$

D.Z. brand diesel fuel, derived from Baku petroleum, and boiling off within a range from 190 to 330°, was subjected to oxidation. The oxidation was carried out at a reactor pressure of 700 mm Hg, a temperature of 100-500°, and drop dimensions of 0-1.4 mm. The time spent by the fuel drops in the reactor was determined by computation [6] and amounted to ~ 0.07 sec. The time spent by the fuel vapors in the reactor was equal to ~ 1 sec. The results of the investigation showed that under the given conditions the fuel vapors remained virtually unoxidized. At the same time, the fuel drops were subjected to intensive oxidization despite the substantially shorter time that they spent in the reactor (Figs. 35, 36).

The oxidation of the fuel drops – a heterogeneous chemical process whose rate is a function of the rate of oxygen diffusion to the surface of the drop. With an increase in the air temperature, the rate of oxygen diffusion to the surface of the drop increases. Simultaneously, there is an increase in the quantity of fuel vaporized from the surface of the drop. The formed flow of fuel vapors diffuses from the surface of the drop and offers resistance to the approaching oxygen diffusion. Therefore a change in temperature within the range from 100 to 500° exerts comparatively little influence on the quantity of oxidized molecules (Fig. 35). A similar situation is observed in the case of a reduction in drop diameter. Here we also observe, on the one hand, an increase in the rate of the reaction as a result of the increase in surface area per unit volume; on the other hand, an increase in surface area per unit volume of substance results in an increase, according to the B.I. Sreznevskiy [7] law, in an increase in the quantity of vaporized fuel. The total effect of these processes results in a reduction of the degree of oxidation, beginning with drops having a diameter of ~ 1.0 mm.

The data that we obtained make it possible for us to expect rather intensive oxidation of the drops under the conditions prevailing in the engine. Drops of atomized fuel (of all dimensions) are subjected to some oxidation, even at rather low temperatures. The data presented in Figs. 35 and 36 were obtained at a pressure of 700 mm Hg. At higher engine pressures, the rate of oxygen diffusion in the drop increases and there is a simultaneous reduction in the quantity of fuel vaporized from the surface of the drop. All of this leads to the pronounced intensification of fuel-drop oxidation.

In the other experiments, the results of which are presented in Fig. 37, we established a relationship between the oxidizability of drops of DZ diesel fuel to which various quantities of organic peroxide had been added and the cetane number (or the ignition lag) of the diesel fuel containing various quantities of organic peroxide.

The duration of the ignition lag for the fuel is determined by the rate of the preflame reactions. In the case of autoignition of fuel-air mixtures under the conditions prevailing in the high-temperature zone, the addition of small quantities of peroxide compounds has no significant effect on the rate of the preflame reactions, since the peroxide compounds in this case are not the substances which determine the degenerate branching of the chains. The addition of peroxide compounds to the fuel under the conditions prevailing in a diesel engine may accelerate only the preflame reactions taking place in the liquid phase, i.e., the oxidation reaction of the atomized fuel drops. The results that we obtained are presented in Fig. 37 and indicate the significant effect that the liquid-phase oxidation of fuel drops exerts on the rate of preflame reactions in the case of fuel autoignition in a diesel engine.

## FUEL COMBUSTION IN DIESEL ENGINES

Compression-ignition (diesel) engines refer to piston engines in which air is compressed in cylinders and the fuel injected into the cylinder at the end of the compression stroke is ignited as a result of high air temperature.

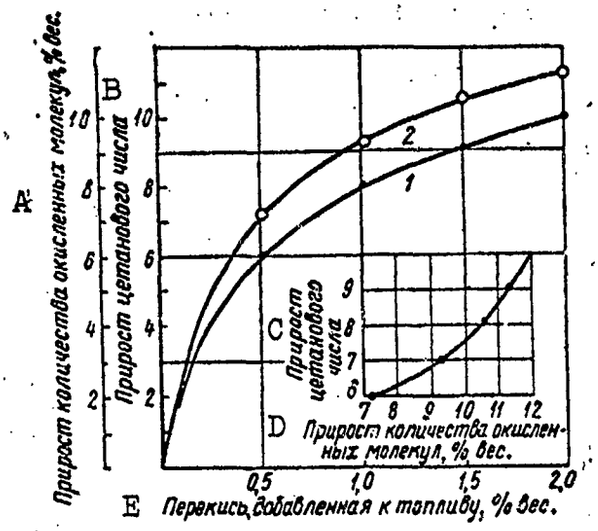


Fig. 37. Effect of addition of organic peroxide on change of cetane number (1) and on degree of liquid-phase fuel-drop oxidation (2). A) Increment in quantity of oxidized molecules, % by weight; B) increment in cetane number; C) increment in cetane number; D) increment in quantity of oxidized molecules, % by weight; E) peroxide added to fuel, % by weight.

The air pressure in the cylinder of a diesel engine at the end of the compression stroke attains 30-40 kg/cm$^2$. Here the air temperature rises to 550-650°. Such parameters in the diesel engine are attained as a result of a high compression ratio, equal to 13-18.

The fuel is sprayed (injected) into the cylinder of the diesel engine under a pressure of 200-700 kg/cm$^2$. The fuel enters in the form of small drops having dimensions of 5-100μ.

The supply of fuel to the cylinder of the engine begins some 10-20° of crank-angle rotation before top center and continues as the crankshaft turns through an angle of 20-35°. In this case, the following fuel-supply function is achieved (the time distribution of the fuel being supplied during the injection period): during the first and last quarter of the injection period ~ 25% of the total quantity of fuel injected during the cycle is supplied. The remaining quantity of ~ 75% is supplied during the second and third quarters.

The fuel-combustion process in a diesel engine is generally divi-

ed into three phases.

The first phase occupies the time interval from the instant of the beginning of fuel injection to the instant of the beginning of a pressure rise as a result of the fuel ignition that took place. This time period is defined as the autoignition lag. In the case of high-speed diesel engines, the duration of the ignition lag is (0.5-2) x x $10^{-3}$ sec.

The duration of the ignition lag (of the first phase) is primarily a function of the chemical and physical properties of the fuel, and the temperature and pressure of the compressed air.

During this period of time the preflame reactions occur within the fuel, and these in the final analysis result in the autoignition of the fuel.

The duration of the ignition lag determines the quantity of fuel which will be consumed in the engine as a result of autoignition. The greater the ignition lag, the greater the quantity of fuel entering the cylinder of the engine in time for ignition, and the greater the portion of the fuel consumed as a result of autoignition.

The second phase begins with the instant of ignition and continues to the instant at which the maximum pressure of the cycle is attained. During the second phase the fuel which had entered the engine in time for ignition is consumed, as is that portion of the fuel which continues to enter the combustion chamber during the second phase. The latter is vaporized and consumed as a result of the propagation of the flame from the flame foci that have originated. This portion of the fuel is consumed at a slower rate than that which enters the combustion chamber during the ignition lag and in which, at the instant of ignition, the preflame reactions took place.

By the end of the second phase, the pressure rises to 60-100 $kg/cm^2$.

The rate of pressure increase can attain 6-8 kg/cm$^2$ per 1° of crank angle. The high rate of pressure increase determines the appearance of knocking and "hard" engine operation. It is felt that an engine is operating "softly" at a pressure-rise rate not exceeding 5 kg/cm$^2$ per 1° of crankshaft angle of rotation.

The basic effect on the nature of the fuel-combustion process during the second phase is exerted by the duration of the ignition lag and the quantity of fuel which enters during the ignition lag. However, these quantities determine the rate of pressure increase and the "hardness" of engine operation as well.

The third phase begins at the instant that the maximum pressure is attained and continues until the instant at which 95-97% of the fuel has been consumed. By the beginning of the third phase, the supply of fuel usually ceases. The rate of fuel combustion during this stage is substantially lower than during the second phase, since the combustion takes place under conditions of reduced oxygen concentration, dilution of the combustible mixture by the products of combustion, and under conditions of reduced pressure in the cylinder as a result of the piston shift. The duration of combustion during this phase is determined primarily by diffusion processes.

Conditions for the Most Effective Establishment of the Combustion Process

The economy of the engine is evaluated by the magnitude of the specific fuel consumption, i.e., the fuel flow rate per unit of power, in an hour.

The specific fuel consumption $g_i$ per 1 indicator force in an hour can be calculated from the following equation:

$$g_i = K \frac{P_0 \eta_v}{T_0 P_i a L_0},$$

where $P_0$ and T are, respectively, the pressure and temperature of the

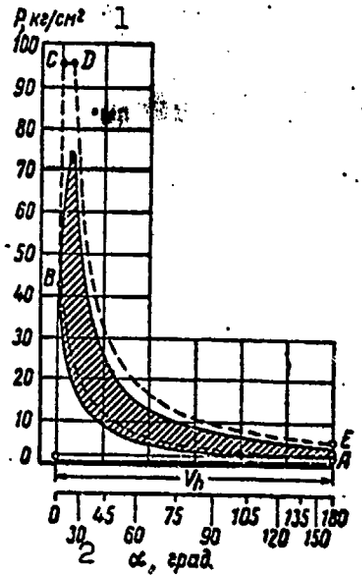


Fig. 38. Theorectical and experimental indicator diagrams, in P-V coordinates. 1) P, kg/cm$^2$; 2) α, deg.

ambient medium; $\eta_V$ is the fill factor; α is the excess air ratio; $L_0$ is the theoretical quantity of air per m$^3$ required for the total (complete) combustion of 1 kg of fuel at 15° and 735 mm Hg; $P_i$ is the mean indicator pressure – the conditional excess constant pressure – which acts continuously on the piston during the course of a single stroke and accomplishes work equal to the indicator work during a cycle; K is a proportionality factor. *

In Eq. (1) the indicator which is a function of the nature of the combustion process is $P_i$. Figures 38 and 39 show the indicator diagrams of ideal and real cycles in the following coordinates: PV (pressure and volume) and P-α (pressure and the angle of crankshaft rotation).

The mean indicator pressure of an actual cycle can be calculated in terms of the magnitude of the hatched area S (Fig. 38): $P_i = S/V_h$.

The greater the area S or an equivalent area bounded by the curve bcdeb (Fig. 39), the greater the value of $P_i$ for a constant cylinder volume $V_h$.

The value of the area S will be at its maximum upon completion of the theoretical cycle, i.e., as the pressure in the engine cylinder changes in accordance with the curve ABCDE (Fig. 39). Because of engine heat losses brought about by heat transfer, the peculiarities and incompleteness of combustion, and hydraulic losses, the actual indicator diagram (bcdeb) differs from the theoretical.

The extent to which the actual indicator diagram can be approxi-

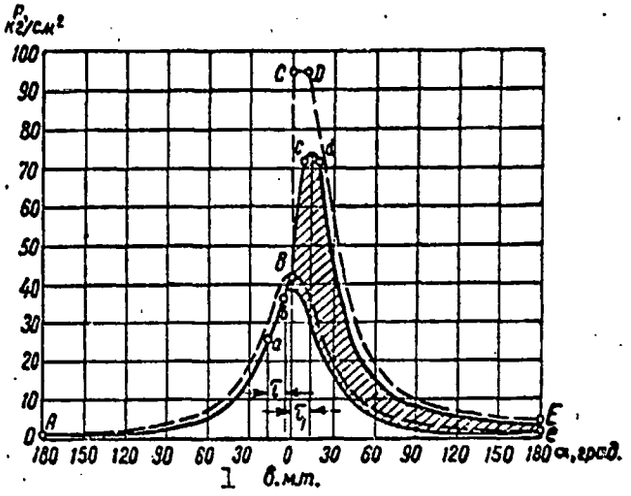


Fig. 39. Theoretical and experimental indicator diagrams, in P-α coordinates. 1) Top center.

mated to the theoretical indicator diagram is also limited by the permissible rate of pressure increase. A condition necessary for the completion of fuel combustion in accordance with the theoretical indicator diagram is the instantaneous increase in pressure at top center (line BC, Fig. 39). This type of explosive fuel combustion results in the rapid destruction of the engine.

The dimension of the area bcdeb, and consequently, the dimension of $P_i$ is a strong function of the instant at which the fuel ignites as well as of the quantity of fuel that enters the engine cylinder at the instant of ignition.

We can employ the data presented in Fig. 40 to arrive at a conclusion as to the effect exerted by the instant of fuel ignition on the dimension of the indicator diagram. As we can see from Fig. 40, the greatest indicator-diagram area dimensions are attained in the case of fuel ignition at top center or close to top center.

We can employ the data presented in Fig. 41 to arrive at a conclusion as to the nature of the effect exerted by the quantity of

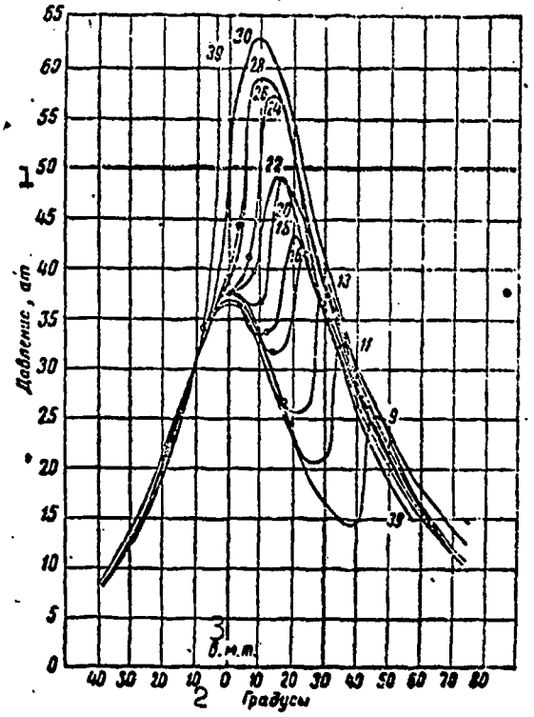


Fig. 40. Change in indicator diagram as a function of the crank-angle lag (the numbers on the diagram indicate the values of the injection crank-angle lag). 1) Pressure, atm; 2) degrees; 3) top dead center.

injected to the instant of ignition on the indicator-diagram area.

Given identical fuel feed during the cycle, the greater the amount of fuel entering the engine cylinder to the instant of ignition, the greater the area of the indicator diagram.

Given constant injection crank angles and a fuel-supply function, the instant of fuel ignition and the quantity of fuel injected into the engine cylinder to the instant of ignition are determined by the duration (extent) of the ignition lag.

The instant of fuel ignition is determined by the difference between the duration $\tau$ of the ignition lag and the injection crank-angle lag $\theta$. If $\tau > \theta$, the fuel ignites beyond top center, and this reduces the area of the indicator diagram and $P_i$. If $\tau$ is equal to or somewhat less than $\theta$, the area of the indicator diagram and $P_i$ have a greater value.

If, however, $\tau$ is substantially less than $\theta$, the fuel will ignite and begin to burn long before the piston reaches top center and a portion of the engine power will be wasted on overcoming the pressure developed as a result of the combustion of a part of the fuel during the compression stroke, and this will make itself felt in reducing the

economy of the engine.

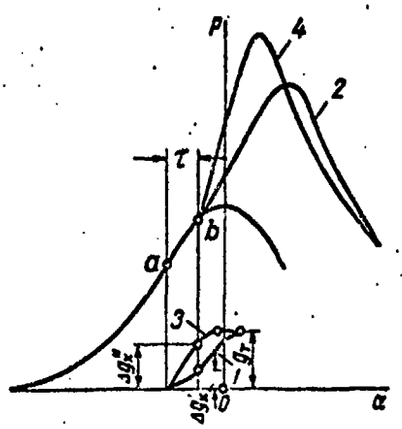


Fig. 41. Change in indicator diagram as a function of the quantity of fuel injected into the cylinder to the instant of ignition. 1-3) Fuel-supply function; 2 and 4) indicator diagrams corresponding to curves 1 and 3; $g_t$) total quantity of fuel injected into cylinder; $\Delta g_x'$ and $\Delta g_x''$) quantity of fuel injected to instant of ignition in the case of fuel feed according to functions 1 and 3.

An increase in $\tau$ will result in an increase in the quantity of fuel injected into the engine cylinder to the instant of ignition. In this case, a greater part of the fuel charge is subjected to preflame preparation. As a result, at the instant of ignition there appear a great many flame foci and the combustion takes place more intensely and at a higher rate of pressure increase, and this reduces the time during which maximum combustion pressure is attained, and it also increases the time required for the complete combustion of the fuel. Therefore with an increase in $\tau$ the area of the indicator diagram and $P_i$ increase, and consequently, there is an increase in engine economy.

The economy of the engine can be increased only to the limit determined by the value of $\tau$ at which the rate of pressure increase and the maximum combustion pressure attain their limit values.

With a decrease in $\tau$ we will find the opposite situation. Consequently, the ignition lag for the fuel is a basic indicator which determines the promptness of fuel ignition and combustion.

The requirement for prompt ignition and combustion of the fuel can be satisfied if the following conditions are observed.

1. For a given fuel-supply function, the duration of the ignition lag must provide for the injection of a quantity of fuel into the cyl

cylinder to the instant of ignition as can burn up at the maximum permissible rate of pressure increase.

2. The fuel must ignite close to top center, and this can be achieved by the appropriate setting of the fuel-injection crank-angle lag.

Preflame Processes in a Diesel Engine

As a result of having been heated in the fuel-feed pump and in the fuel manifold, the fuel injected into the combustion chamber of the diesel engine has a temperature of 60-100°. After vaporization, the fuel is heated to the temperature of the compressed air ( ~ 500°).

If we assume that the preflame reactions take place only in the vapor phase, ignition must be of the single-stage variety, since in this case there is no change in the mechanism of the degenerate branching of the chains. At the same time, however, there are numerous experimental data indicating the existence of multistage fuel ignition in a diesel engine and, consequently, indicating preflame reactions in which, with the passage of time, a change in the mechanism of the degenerate branching takes place and this change is accompanied with the appearance of "cold flames."

The multistage aspects of ignition in a diesel engine can be explained if we take into consideration the possibility of liquid-phase oxidation of drops of atomized fuel. In this case the preflame processes taking place within the combustion chamber of the diesel engine can be presented in the form of the following basic reactions (Table 18).

We can see from Table 18 that the autoignition of atomized liquid fuel takes place in three stages.

The first stage occupies the time interval from the instant of fuel injection to the instant of fuel vaporization. Slight liquid-phase

TABLE 18

Basic Chemical Reactions for Preflame Fuel Preparation in a Diesel Engine

| 1 Стадия самовоспламенения | 2 Фазовое состояние топлива | 3 Основные реакции | |
|---|---|---|---|
| | | 4 продолжения цепи | 5 вырожденного разветвления |
| 6 1-я | 9 Жидкое | $\dot{R}+O_2 \rightarrow R\dot{O}O$<br>$R\dot{O}O+RH \rightarrow ROOH+\dot{R}$ | $ROOH \rightarrow R\dot{O}+\dot{O}H$ |
| 7 2-я | 10 Паровое | $ROOH \rightarrow R\dot{O}+\dot{O}H$<br>$\dot{O}H+RH \rightarrow \dot{R}+H_2O$<br>$R\dot{O}+RH \rightarrow \dot{R}+R'CHO$ | $RCHO+O_2 \rightarrow R'C\dot{O}+H\dot{O}_2$<br>$CH_2O+O_2 \rightarrow HC\dot{O}+H\dot{O}_2$ |
| 8 3-я | Паровое | $R\dot{O} \rightarrow R''CH_2O \rightarrow \dot{R}''+CH_2O$<br>$R'C\dot{O}+RH \rightarrow R'CHO+\dot{R}$<br>$R\dot{O}O \rightarrow R'\dot{O}+R''CHO$ | |

1) Autoignition stage; 2) fuel phase; 3) basic reactions; 4) continuation of chain; 5) degenerate branching; 6) first; 7) second; 8) third; 9) liquid; 10) vapor.

oxidation of fuel drops takes place during this stage. Hydrogen peroxide is the substance which causes the degenerate branching of the chain oxidation reaction.

The second stage of the process begins at the instant of fuel vaporization and continues to the instant of intensive destruction of the peroxide compounds formed during the oxidation of the fuel in the liquid phase.

This instant of intensive decomposition of the peroxides and the formation of a high concentration of radicals is commonly, apparently, associated with the appearance of the cold flame. The latter may serve as an indication of the completion of this stage. During the second stage a small quantity of aldehydes is formed, and these determine the subsequent degenerate branching of the chain oxidation reaction in this stage.

The third stage begins at the instant that the cold flame appear and lasts until the instant of the appearance of a hot flame. Th[illegible]

tensive oxidation reactions, with the branching of the chains through the aldehydes, continue during this stage.

Consequently, the multistage aspects of the autoignition process in the diesel engine are attributable to the stage of the liquid-phase oxidation of the drops of atomized fuel. In those cases in which this stage plays an insignificant role, i.e., for example with extremely high fineness of atomization or at an extremely high compressed-air temperature and low pressure, in which case the fuel drops vaporize at a high rate, single-stage ignition is possible. The transition of the autoignition of atomized fuel from multistage to single-stage processes was observed, for example, in Reference [10].

The autoignition of a fuel in a diesel engine differs in nature from the autoignition in a spark-ignition engine. In the case of fuel autoignition in a spark-ignition engine we note the appearance of compression waves and the appearance of "detonation" combustion. In the case of a diesel engine, the autoignition of the fuel does not exhibit this "detonation" feature. The knocking which occurs in a diesel engine at high "hardness" of operation, is superficially different from detonation (knocking) in spark-ignition engines. In the case of detonation (knocking) there is a drop in power, exhaust smoke, an increase in the specific fuel consumption, and overheating of individual points of the combustion chamber. Knocking in diesel engines, on the other hand, is accompanied by an increase in power and a reduction in the specific fuel consumption as a result of the greater "hardness" of engine operation. In the case of engine operation with knocking, no local overheating of component parts is observed.

In Reference [11] the distinction between the autoignition processes in diesel and spark-ignition engines was demonstrated by utilization of a method of motion-picture recording of the propagation of

a flame in the cylinder of a diesel engine as well as in the cylinder of a spark-ignition engine. With autoignition in a diesel engine no shock waves were observed, whereas these are characteristic of autoignition in a spark-ignition engine. Autoignition in the diesel engine was accompanied by the appearance of a great quantity of initial flame foci from which the flame propagated through the entire fresh mixture at great speed.

We pointed out earlier that one of the means of increasing engine efficiency is to increase the quantity of fuel consumed as a result of autoignition. As we shall see, because of certain factors the quantity of fuel that can be consumed in engines as a result of autoignition is limited. In diesel engines this limitation is associated with the permissible rate in the pressure rise. The preflame reactions taking place in a diesel engine are not factors which limit the quantity of fuel that can be consumed as a result of autoignition.

## FEATURES IN THE COMBUSTION OF FUEL IN ENGINES OPERATING ACCORDING TO THE "M-PROCESS"

Until recently, designers ascribed a decisive role to mixture formation during the combustion process in their development of diesel engines. It was assumed that in order to attain the greatest economy, as well as noiseless and smoke-free exhaust operation of the diesel engine, rather fine atomization of the fuel and uniform fuel distribution in the combustion chamber are required. However, the investigations carried out in this direction have shown that to attain the rapid mixing of fuel with air and uniform distribution of the fuel-air mixture in the combustion chamber, conversely, results in a pronounced intensification of "knock" in the engine, as well as in the poor utilization of the air and the appearance of intensive exhaust smoking in all regimes [12-15].

Moyrer [sic] [13-15] adopts an entirely different approach to the achievement of the combustion process in a diesel engine.

The basic feature of this method of carrying out the combustion process involves the fact that the fuel is injected by means of a special two-orifice spray nozzle which atomizes a small quantity of the fuel (5%) into heated air, and injects a greater portion of the fuel against the wall of a hemispherical combustion chamber in the piston. The fuel is distributed over the surface of the combustion chamber in the form of a liquid film having a thickness of ~ 12 μ. The bottom plate of the combustion chamber is intensively cooled with oil so that the temperature of the wall against which the fuel is sprayed does not exceed 340°. That portion of the fuel (5%) atomized in hea ed air ignites and serves as the ignition flame for the remaining portion of the fuel which vaporizes from the wall of the combustion chamber.

The described method of combustion has been designated as the "M-process." Engines operating in accordance with the "M-process" were first produced by the MAN Company, and then by others. It turned out that these engines exhibited high economy, operating noiselessly ("whispering" engines) and with limited exhaust smoke. A unique and particularly important advantage, from a practical standpoint, of this engine is its "omniverous nature": it functions equally well on diesel fuel and on gasolines.

These features of fuel combustion in an engine operating according to the "M-process" are a result of the sharp reduction in the quantity of fuel consumed as a result of autoignition.

Proceeding from the general considerations, we spoke above of the feasibility of reducing the quantity of fuel which enters the combustion chamber to the instant of ignition. However, in the general exe-

cution of the combustion process in a diesel engine the time for the ignition of the basic fuel mass is reduced, and this results in substantial incompleteness of fuel combustion.

In the "M-process" a small portion of the fuel being ignited is injected simultaneously with the basic fuel mass, and this does not reduce the time required for the combustion of the basic fuel mass.

The thin film of fuel on the surface of the combustion chamber is subject to intensive liquid-phase oxidation. Favorable conditions for liquid-phase oxidation prevail, first of all, because of the lower volatility of the fuel film in comparison with the volatility of the atomized fuel and, secondly, the metallic wall of the combustion chamber exerts a catalytic effect, accelerating the oxidation process.

Under these conditions, even fuels that vary in terms of molecular structure undergo rather intensive oxidation.

The oxidized fuel film gradually vaporizes. The fuel (combustible) vapors that are formed are ignited by the flame of the ignited fuel. Subsequently, the mixture is consumed primarily as a result of the propagation of the flame from the ignition source. Fuels with various molecular structures have no significant effect on the combustion process under these conditions.

FUEL COMBUSTION IN SPARK-IGNITION ENGINES

There are two types of engines with spark ignition – with internal mixture formation (direct-injection engines) and with external mixture formation (carburetor engines).

Mixture formation through the direct injection of fuel is accomplished by means of a multi-section (in terms of the number of cylinders) pump. The fuel is injected either into the engine cylinder or into a special antechamber or fuel collector from where it is drawn into the engine cylinder. This type of engine was used only on a lim...

ed scale because of its great complexity and high cost in comparison with carburetor engines.

In engines with external mixture formation the fuel is atomized by the carburetor. In contemporary engines, the rate of air flow through the carburetor diffuser attains 150 m/sec with a pressure difference (the difference in pressure between atmospheric and the pressure in the diffuser) of up to 0.2 kg/cm$^2$.

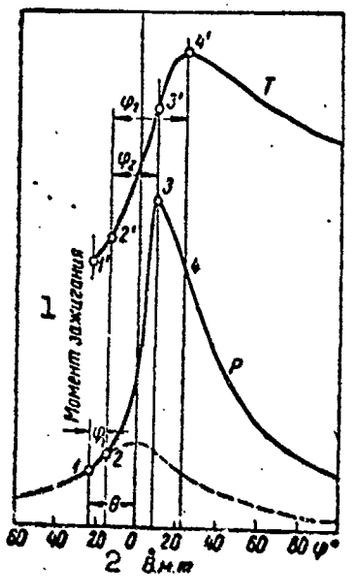


Fig. 42. Diagram showing change in pressure P and temperature T in spark-ignition engine as a function of the angle of crankshaft rotation [9]. 1) Instant of ignition; 2) top dead center.

The atomized fuel leaves the carburetor and enters the ignition collector which has been heated from the outside by the exhaust gases, and up to 60-80% of the fuel is vaporized here. That portion of the fuel which did not vaporize enters the engine cylinders in the form of a film and vaporizes in the cylinders. The mixture of fuel vapors with air is compressed by a piston and as the piston reaches a position 20-30° before top center (the crank-angle ignition lag), a spark jumps across the electrodes of the sparkplug and the mixture is ignited.

A typical diagram of the change in pressure and temperature in the cylinder of a spark-ignition engine as fuel is being burned up is presented in Fig. 42 (the GAZ-51 engine). According to the indicator diagram, the combustion of the fuel in the spark-ignition engine is generally divided into three stages.

The first stage – the ignition lag begins from the instant of spark appearance in the sparkplug (point 1, Fig. 42) and ceases at the instant that there appears a pronounced increase in pressure. The ini-

tial combustion focus forms during this stage, and this corresponds to the combustion of 6-8%, by volume, of the mixture. Therefore the ignition lag in this case is composed of an induction period of ignition and the time required for the formation of the initial combustion focus.

Unlike a diesel engine, the ignition lag in a spark-ignition engine is not directly associated with the rate of pressure increase.

The second stage is the stage of basic heat liberation from the instant at which the rise in pressure begins (point 2, Fig. 42) to the instant at which maximum pressure is attained (point 3, Fig. 42). In this stage, the flame is propagated almost throughout the entire volume of the mixture at a rate of 15-40 m/sec. The rate of fuel combustion during this stage is a function of the compression ratio, of the crank-angle ignition lag, the composition of the mixture, and similar factors (the shape of the combustion chamber, the disposition of the sparkplugs, the intensity of vortex formation, etc.).

The third stage is the stage of complete combustion at the expansion line (points 3 and 4, Fig. 42).

Conditions for the Most Economical Establishment of the Combustion Process in a Spark-Ignition Engine

The economy of a spark-ignition engine, just as of a diesel engine, can be evaluated in terms of the specific fuel consumption $g_i$:

$$g_i = \frac{KP_0\eta_V}{T_0 P_i\left(\alpha L_0 + \frac{1}{m_t}\right)}, \qquad (2)$$

where $\alpha L_0 + (1/m_t)$ is the number of kg-mole of the fuel (combustible) mixture per 1 kg of fuel (propellant).

The remaining indicators are the same as in Formula (1). In this equation $P_i$ is also the basic indicator which is a function of combustion.

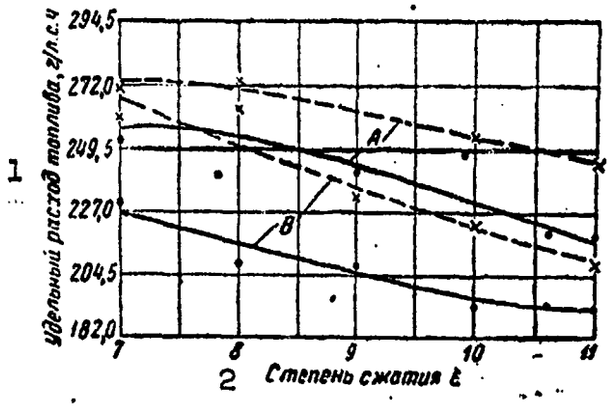


Fig. 43. Effect of compression ratio on specific fuel consumption for various carburetor settings [37]. A) Power setting; B) economical setting; —— 2000 rpm; x – x – x 4500 rpm; 1) Specific fuel consumption, g/hp·hr; 2) compression ratio.

For an engine with a spark ignition the conditions of maximum economy formulated earlier for a diesel engine remain valid, i.e.: 1) the ignition of the fuel with a specified ignition lag must take place close to top center; 2) during the second stage the rate of pressure increase must be the maximum permitted by the design of the engine.

It is easy to achieve the first condition in a spark-ignition engine by making the appropriate ignition settings and by employing regulators that automatically establish the optimum value for the crank-angle ignition lag as a function of the composition of the mixture.

The situation is somewhat different in the case of the second condition.

The basic design parameter affecting the rate of pressure increase is the compression ratio. In contemporary engines, for a compression ratio of 6.5-8.0, the rate of pressure increase is equal to 1.1-1.6 $kg/cm^2 \cdot deg$. As we can see, in an engine with spark ignition the value

of the pressure-increase rate is many times smaller than in the case of diesel engines. An increase in the compression ratio makes it possible substantially to increase $P_i$ and correspondingly it makes it possible to increase the economy of the engine (Fig. 43). However, the possibility of using this method to increase the economy of a spark-ignition engine is restricted by the quality of the fuel. It turns out that with an increase in the compression ratio above a certain specified limit, constant for each grade of fuel, "knocking" will appear in the engine, power will be reduced, the engine will overheat, and black smoke will appear in the spent gases. It was quickly established that the factor responsible for the origination of "knocking" is the extremely rapid propagation of the flame in the last part of the charge. The rate of flame propagation in the case of intensive knocking corresponds to a detonation or explosion wave (~ 2000 m/sec).

Detonation Propagation of Flame

In 1881, a number of investigators, studying the propagation of a flame in gaseous mixtures contained in cylindrical tubes (Mallard, Le Chatelier [16], Berthelot, Vieille [17]) observed an interesting phenomenon.

The first instant after the ignition of the mixture, the flame slowly propagates through the tube and then the rate of this propagation increases to extremely high values which subsequently do not change. The maximum rate at which the flame is propagated was constant for each gas mixture and attained 1500-3500 m/sec. This phenomenon of flame propagation at such a fast speed was designated as "detonation" or "detonation propagation" of a flame. Subsequent research made it possible to establish a number of specific features of this phenomenon. For example, detonation propagation of a flame was observed only in mixtures characterized by a high normal rate of flame propagation. The

TABLE 19

Concentration Limits for Propagation of Detonation at Initial Pressure of 1 atm and Room Temperature [20]

| | 1 Смесь | 2 Содержание горючего в окислителе, % | | 5 Скорость детонации, м/сек | |
|---|---|---|---|---|---|
| | | 3 нижний предел | 4 верхний предел | 6 на нижнем пределе | 7 на верхнем пределе |
| 8 | $H_2$—$O_2$ | 20 | 90 | 1457 | 3550 |
| 8 | $H_2$—воздух | 18,2 | 58,9 | 1500 | 2100 |
| 10 | CO—$O_2$ (сухая) | — | 83 | — | — |
| 10 | CO—$O_2$ (влажная) | 38 | 90 | — | 1473 |
| 11 | (CO+$H_2$)—$O_2$ | 17,2 | 90 | 1500 | 2150 |
| 11 | (CO+$H_2$)—воздух | 19 | 58,7 | 1488 | 1690 |
| 12 | $C_2H_4$—воздух | 5,5 | 11,5 | 1675 | 1801 |
| 13 | $C_2H_2$—$O_2$ | 3,5—3,6 | 92—93 | 1607 | 2423 |
| | $C_2H_2$—воздух | 4,2 | 50 | 1509 | 1871 |
| | $C_2H_6$—$O_2$ | 3,2 | 37 | 1587 | 2210 |
| | $i$-$C_4H_{10}$—$O_2$ | 2,9 | 31,3 | 1505 | 2188 |
| 14 | $(C_2H_5)O$ эфир—$O_2$ | 2,7 | 40 | 1593 | 2323 |

1) Mixture; 2) content of fuel (combustible) in oxidizer, %; 3) lower limit; 4) upper limit; 5) rate of detonation, m/sec; 6) at lower limit; 7) at upper limit; 8) $H_2$ – air; 9) CO – $O_2$ (dry); 10) CO – $O_2$ (moist); 11) (CO + $H_2$) – air; 12) $C_2H_4$ – air; 13) $C_2H_2$ – air; 14) $(C_2H_5)O$ [sic] ether – $O_2$.

rate of detonation changed with a change in the composition of the mixture. Limit values for the composition of the mixture were noted, and above or below these limits the mixture did not detonate (Table 19). Here the concentration limits of detonation or the "detonation boundaries" were narrower than the ignition boundaries. The rate of detonation went virtually unchanged with a change in the tube diameter (if it is greater than some small value), nor did it change as a result of a change in the curvature of the tubes, the initial pressure, the temperature of the mixture, or the conditions prevailing behind the front.

The very first investigators of the phenomenon of detonation offered a valid explanation for it [16, 18].

The detonation wave was regarded as a shock wave in which a rather high temperature develops, leading to the autoignition of the adjacent

mixture layers. Proceeding from this concept of the nature of detonation, the investigators developed the fundamentals of the theory of detonation, referred to as hydrodynamics [16, 19, 20].

Using this theory, the investigators calculated the detonation rates for gas mixtures in tubes and found that these agreed well with the experimentally determined values. The agreement of the theoretically calculated and experimental values for the detonation rate confirms the validity of the concepts on which the hydrodynamic theory of detonation is founded.

The hydrodynamic theory of detonation presupposes the following mechanism for the formation of a powerful shock wave in the propagation of a flame in tubes. The combustion of a gas is accompanied by the expansion of the products of combustion which act on the flame front, accelerating its propagation. With each small acceleration of the motion of the flame, a weak compression wave moves away from the flame front. In this case, each subsequent compression wave moves at a velocity greater than the velocity of the preceding wave, and this is due to the heating of the medium by the preceding wave; Therefore the second wave overtakes the first wave. As a result, at some distance from the point of ignition the waves merge into a powerful shock wave resulting in the detonation of the mixture. The distance L from the point of mixture ignition in the tube to the point of detonation can serve as a measure for the evaluation of the tendency of various gas mixtures to detonate. Tables 20 and 21 present data on changes in L as a function of the chemical composition of the mixture, the initial pressure, and the temperature of the mixture.

From Tables 20 and 21 we can see that the parameter L is more sensitive to changes in the initial conditions in the detonating mixture as well as to changes in the chemical composition of the detonating

TABLE 20

Effect of Pressure on Distance from Point of Ignition to Point of Detonation in Various Mixtures [21]

| 1 Смесь | 2 Расстояние в см при давлении, мм рт. ст. | | | |
|---|---|---|---|---|
| | 80 | 100 | 200 | 300 |
| $2H_2+O_2$ | — | — | 78 | 52 |
| $CH_4+2\,O_2$ | — | 134 | 78 | 51 |
| $C_2H_6+3{,}5\,O_2$ | — | 102 | 58 | 46 |
| $C_4H_{10}+9{,}5\,O_2$ | 105 | 48 | 32 | 27 |
| $C_6H_6+7{,}6\,O_2$ | — | 54 | — | 47 |

1) Mixture; 2) distance in cm, at pressures in mm Hg.

TABLE 21

Effect of Initial Temperature on Distance from Point of Ignition to Point of Detonation [22]

| 1 Смесь | 2 Начальная температура, °С | L, см |
|---|---|---|
| $2H_2+O_2$ | 15 | 60 |
| | 120—130 | 73 |
| | 160—180 | 3 78 |
| | 300—320 | В метровой трубе детонация не возникает |
| $CH_4+2O_2$ | 15 | 55 |
| | 160—180 | 74 |
| | 290—310 | 80 |
| | 340—350 | В метровой трубе детонация не возникает |

1) Mixture; 2) initial temperature, °C; 3) in a meter-long tube there is no detonation.

mixture than is the rate of detonation. With an increase in the temperature of the mixture, L increases and with an increase in pressure, L diminishes. The parameter L increases with an increase in the diameter of the tube and diminishes with an increase in the degree of tube-wall roughness.

Flame acceleration in the predetonation can be brought about not only through the influence of the "ejecting" effect of the expanding

products of combustion on the flame front. For example, K.I. Shchelkin ascribes the dominant role here to the "turbulization" of the flame front, as a result of which there is a pronounced increase in the rate of flame propagation, which in turn increases the degree of turbulence [23].

In addition to the phenomenon of detonation flame propagation examined above, we encounter special cases of detonation. For example, in hard-to-detonate mixtures or in mixtures close in terms of composition to the limit, we encounter the phenomenon of detonation spin [24, 25]. The phenomenon of vibration combustion, generally preceding detonation, can be assigned to the case of a weakly expressed detonation.

The above-described phenomenon of detonation is observed in the propagation of a flame through uniform gas mixtures in long smooth tubes and characterized by a high normal rate of flame propagation.

Detonation Combustion in a Spark-Ignition Engine

The investigations that have been carried out in order to clarify the factors responsible for the origination of detonation combustion in spark-ignition engines resulted in the establishment of a definite link between the chemical structure of the fuel molecules and the appearance of "knocking." The operation of an engine with a variable compression ratio on n-paraffinic (n-heptane) and isoparaffinic (isooctane) hydrocarbons, detonation combustion takes place in the first case at a low compression ratio, and in the second case at a substantially higher compression ratio. It was found that the addition of a small quantity of certain substances (antiknock additives) prevents the occurrence of "knocking," and the addition of other substances (peroxides) enhances the occurrence of "knocking." The use of photographic recording methods showed that "knocking" occurs as a result of autoignition and the instantaneous detonation combustion of the last part of the fuel charge

entering the combustion chamber. These investigation results led to the conclusion that the factors responsible for the appearance of detonation combustion in spark-ignition engines should be sought in the features of the preflame chemical reactions taking place in the last part of the fuel-air-mixture charge.

The first detonation theories proceeded from the known experimental fact that the addition of a peroxide reduces the magnitude of the compression ratio at which "knocking" takes place, and these theories associated the occurrence of detonation (knocking) with the explosive decomposition of the peroxides formed in the oxidation of the fuel in the combustion chamber of the engine. Subsequently, with the development of the theory of chain reactions and investigations of oxidation and ignition of hydrocarbon-air mixtures, the peroxide theory of detonation underwent further development. The works of A.S. Sokolik, M.B. Neyman, and other investigators demonstrated that the occurrence of detonation in a spark-ignition engine is associated with the multistage aspects of the ignition of hydrocarbon-air mixtures [26-28].

The most logically evolved theory of detonation was proposed by A.S. Sokolik [29]. According to this theory, a detonation wave comes into being in an engine as a result of the formation of a high concentration of active particles - radicals and atoms - in the volume of the mixture which burns during the last stage (the last portion of the charge), and this results in the instantaneous autoignition of this volume of the mixture.

The autoignition of the last portion of the fuel-air-mixture charge takes place in three stages, in accordance with the change in the temperature of the mixture. The first stage begins at the instant of mixture ignition by means of a spark and concludes with the appearance of the primary cold flame in the unconsumed portion of the mixture.

The formation of the cold flame in this stage is associated with the explosive decomposition of the accumulated peroxides in the mixture. As a result of the propagation of the cold flame, 5-10% of the mixture reacts and forms a large quantity of highly active compounds – peroxides, aldehydes, and radicals. After a certain interval of time subsequent to the appearance of the primary cold flame in the mixture, a secondary cold flame appears (the second stage). As a result of the propagation of the secondary cold flame ~50% of the unconsumed mixture reacts. The temperature of the mixture rises. The concentration of CO and of active particles increases in the mixture, and this results in the appearance of a hot flame and the instantaneous combustion of the CO and the unconsumed volume of the mixture, which is equivalent to the formation of a detonation wave (third stage).

From the standpoint of the concepts that we discussed above with respect to the features encountered in the course of the preflame reactions in hydrocarbon-air mixtures, there exists the possibility of providing yet another explanation of the factors responsible for the occurrence of detonation combustion in spark-ignition engines. *

The fuel-air mixture entering the spark-ignition engine cylinder is compressed during the compression stroke. At the end of this compression stroke the temperature and pressure of the mixture increase. After ignition of the mixture by means of a spark and the consumption of a part of the mixture, the unconsumed part of the mixture is subjected to further compression and a rise in temperature. Depending on the temperature and pressure within this portion of the mixture, preflame reactions take place and these correspond to the reactions of the low-temperature and transition autoignition zones.

As was mentioned earlier, the preflame reactions taking place under the conditions prevailing in the transition autoignition zone

are self-oscillatory and are accompanied by the periodic liberation of heat as a result of which compression waves arise.

Under certain conditions compression waves can accelerate themselves and form a detonation wave.

The speed of compression-wave propagation is associated with the rate of the exothermic reactions taking place within the wave. At a certain critical value of the chemical-reaction rate ($W_k$) the compression waves begin to propagate with an acceleration which results in the progressive increase in the quantity of heat liberated within the wave. This increase in the heat liberated within the wave continues until autoignition of the fuel-air mixture in the wave takes place, after which the formed detonation wave is propagated at a constant speed.

The reaction time for the fuel-air mixture in the wave is an extremely small quantity. Given this limited reaction time, the rate of the reaction is a function of the rate of mutual diffusion between the reacting molecules.

A necessary condition for the exothermic chain reaction of fuel-molecule oxidation to take place is the reaction of the interaction between the hydrocarbon radicals $\dot{R}$ with the oxygen molecule, and this results in the formation of the peroxide radical $R\dot{O}O$. We can expect that the probability of collisions between hydrocarbon radicals and oxygen molecules in the wave will be at a minimum and that it will determine the total rate of the reaction.

The rate (W) of the reaction $\dot{R} + O_2 \rightarrow R\dot{O}O$ can be calculated in accordance with the following equation:

$$W = SZ\exp(-E/RT)\,[\dot{R}][O_2].$$

where $[\dot{R}]$ and $[O_2]$ are, respectively, the concentration of the hydro-

carbon radicals and oxygen molecules; R is the gas constant; Z is the number of double collisions; S is the spatial (steric) factor which determines the probability of bimolecular collisions, as a result of which the reaction takes place; E is the energy of activation for the reaction under consideration – a magnitude not exceeding several kcal/mole.

With such small values for the energy of activation and given the high temperature of the mixture in the wave (T) the value of the term exp (-E/RT) is close to unity and the rate of the reaction will be a function primarily of the magnitude of the steric factor S and the concentrations participating in the reaction of these substances.

Consequently, the total rate of the exothermic reaction in the wave will attain a critical value of $W_k$ which will result in the self-acceleration of the compression waves at a fully determined value of the steric factor and the concentration of $\dot{R}$ and $O_2$.

There are two conditions which when satisfied within a spark-ignition engine will result in the appearance of detonation combustion. The first condition is the one which states that preflame reactions corresponding to the reactions of the transition autoignition zone must take place in the fuel-air mixture; the second condition stipulates that the total rate of the exothermic preflame reactions must exceed a certain critical value.

The first and the second condition can begin to be satisfied only if the temperature and pressure of the mixture attain definite limits. The limit values for the temperature and pressure of the fuel-air mixture (in order to satisfy the first condition) are governed by the boundaries of the transition autoignition zone and in order to satisfy the second condition the aforementioned limit values are governed by the corresponding values of the steric factor and the concentrations

of hydrocarbon radicals and oxygen.

Depending on the compression ratio of a spark-ignition engine, the state of the fuel-air mixture is characterized by definite temperature and pressure values. With a higher compression ratio and, consequently, with an increase in the temperature and pressure of the mixture at the end of the compression stroke, the temperature and the pressure of the last part of the charge are correspondingly increased. So long as the compression ratio of the engine is sufficiently low, the preflame processes taking place in the unconsumed part of the mixture take place under conditions that correspond to the conditions prevailing in the low-temperature autoignition zone. In this case, there is either no autoignition or the entire mixture charge burns up as a result of the propagation of the flame from the ignition spark or a small quantity of the mixture in the last part of the charge burns as a result of autoignition, but in this case there is no formation of compressions waves.

A subsequent rise in the compression ratio of the engine may result in the autoignition of the last part of the mixture charge under conditions corresponding to the conditions prevailing in the transition zone and it may also result in the appearance of weak compression waves. And, finally, at a certain critical value of the compression ratio, the pressure and temperature of the last part of the charge attain values at which the second condition for the occurrence of detonation begins to prevail. The autoignition of the last part of the charge is accompanied with the self-acceleration of the compression waves and the appearance of detonation waves.

The above-discussed concept as to the factors responsible for the occurrence of detonation (knocking) in spark-ignition engines makes it possible to explain certain experimental facts which had not as yet

been satisfactorily explained.

The existence of a relationship between the temperature coefficient of the ignition lag (determined under the conditions prevailing in the transition zone) and the detonation (knocking) properties of fuels becomes understandable.

There is an explanation of the factors responsible for the suppression of detonation (knocking) in the case of intensification in turbulent mixing, as a result of which, on the one hand, there is an increase in that portion of the mixture which burns as a result of flame propagation and, on the other hand, there is a change in the conditions under which the preflame reactions take place.

The differences in the antiknock property of n-paraffinic and isoparaffinic hydrocarbons can be explained, as can the antiknock and "predetonation" effect of such substances as tetraethyllead and organic peroxide.

The n-paraffinic hydrocarbons at high temperatures oxidize more easily and all other conditions being equal higher concentrations of hydrocarbon radicals form in these than do in the isoparaffins. At the same time, because of fewer spatial difficulties, the n-paraffins under comparable conditions are characterized by greater values of the steric factor than are the isoparaffins. These differences result in the fact that the second condition for the occurrence of detonation is met in n-paraffinic hydrocarbons at a lower engine compression ratio.

The addition, to the fuel, of organic peroxides determining the degenerated branching of the chains during the course of the preflame reactions under the conditions prevailing in the low-temperature zone sharply increases the concentration of radicals and aldehydes. Therefore the introduction of peroxides into the fuel also satisfies the

second condition for the appearance of detonation at a lower compression ratio. The addition, to the fuel, of tetraethyllead which interacts with organic peroxide correspondingly makes it possible to increase the compression ratio at which the second condition for the appearance of detonation (knocking) is met.

In conclusion it should be pointed out that if the nature of the preflame reactions in a diesel engine has no effect on the economy of the engine, then engine economy in the case of a spark-ignition engine, as follows from what has been presented above, is to a great extent determined by the conditions under which the preflame reactions take place, and also by the nature of these reactions.

FUEL COMBUSTION IN AIR-REACTION ENGINES (VRD)

VRD (air-reaction engines) can be divided into compressor and compressorless on the basis of the method employed to supply air to the combustion chamber.

The basic types of VRD (air-breathing engines) which have gained practical acceptance are the turbocompressor VRD (TRD) and the direct-flow [ramjet] (compressorless) VRD (PVRD). Diagrams of these types of engines are presented in Figs. 44 and 45. More detailed data can be found in Chapter 20.

In TRD (turbojet engines) the air passes through the diffuser into the compressor where it is compressed. The pressure ratio in the compressor may reach values of 4-8. From the compressor the air enters the combustion chamber. By means of a special spray nozzle (injector) fuel is also fed into the combustion chamber. The fuel-air mixture formed as a result is ignited by means of an electric sparkplug. As a result of the combustion of the fuel, the temperature of the gas in the combustion chamber rises. The gas volume in the combustion chamber is greater than the volume of the air compressed by the compressor. The

gas leaves the combustion chamber and passes through the turbine. A portion of the gas energy is taken by the turbine and used to set the compressor in motion. The excess kinematic energy of the products of combustion produces the reaction thrust.

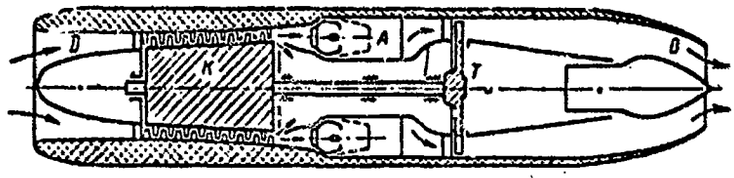


Fig. 44. Diagram of turbojet engine. A) Combustion chamber; D) diffuser; K) compressor; T) gas turbine; B) nozzle.

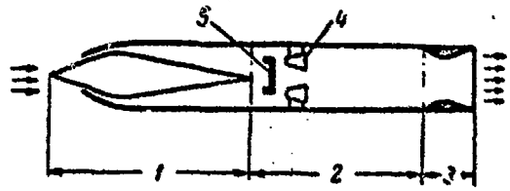


Fig. 45. Diagram of supersonic ramjet VRD. 1) Diffuser; 2) Combustion chamber; 3) nozzle; 4) flameholder; 5) spray nozzle (injector).

The combustion process in TRD (turbojet engines) has two features. The first feature involves the necessity of burning an extremely lean mixture ($\alpha \approx 4.0$), and this makes it possible to provide for a gas temperature of 900-950° at the outlet from the combustion chamber, with this temperature adequate to assure reliable turbine operation. The second feature involves the fact that it is possible to achieve stable combustion in a stream of air moving at a velocity of 40-60 m/sec. In connection with these features, it became necessary to develop special combustion chambers for TRD (turbojet engines). Figure 46 shows a diagram of such a combustion chamber.

A combustion chamber is divided into two zones -- a circulation zone and a zone of complete combustion. The extent of the circulation

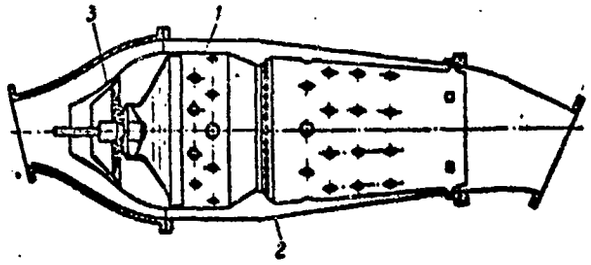


Fig. 46. Combustion chamber of TRD (turbojet engine) with blade swirl chamber. 1) Flame tube; 2) outer chamber; 3) fuel-nozzle ferrule.

zone is approximately equal to the diameter of the chamber. At the forward end of the circulation zone there is a front unit (the fuel-nozzle ferrule). The purpose of this fuel-nozzle ferrule is to stabilize (anchor) the flame. The fuel-nozzle ferrule is most frequently made in the form of a blade swirl chamber.

The air entering the combustion chamber is divided into two streams - a primary and a secondary stream. The primary stream, making up 20-25% of the total quantity of air, enters through the front unit (the fuel-nozzle ferrule) into the circulation zone. As a result, the fuel is consumed in the circulation zone at an excess air ratio close to the stoichiometric. Approximately 50% of the fuel-air mixture is consumed in this zone. The unconsumed part of the fuel burns up in the complete-combustion zone into which the secondary air (75-80%) passes through openings in the flame tube. The secondary stream of air, mixing with the products of combustion, reduces the gas temperature to the levels required to provide for reliable turbine operation (900-950° at the outlet from the combustion chamber). Moreover, the secondary air cools the walls of the chamber's flame tube.

The above-described design of the combustion chamber makes it

possible to provide for stable fuel combustion at high air velocities and a high excess air ratio $\alpha$ exceeding 4.0.

A ramjet VRD consists of an inlet diffuser, a fuel manifold with spray nozzles (injectors), a combustion chamber with an ignition device and a flameholder, and an outlet (exhaust) nozzle. PVRD (ramjet engines) do not produce static thrust. To start a PVRD (ramjet engine) a definite velocity must be imparted to it, and this is accomplished by means of a rocket booster. The approaching air stream is decelerated in the diffuser of the engine, and this increases the static pressure and raises the temperature of the compressed air. The fuel is injected into the stream of air through the injectors of the fuel manifold and this is generally done into the approaching stream. Unlike TRD (turbojet engines) PVRD (ramjet engines) have a zone of mixture formation that is contained between the manifold and the flameholder. The fuel-air mixture is prepared in this zone. Beyond the flameholder the fuel-air mixture is ignited and consumed. The velocity of the outflowing gases exceeds the velocity of the approaching air stream. The increment in momentum obtained in this case results in the reaction thrust of the engine.

PVRD (ramjet engines) are most expediently employed at a flight velocity substantially in excess of the speed of sound (M = 3-4). At these flight velocities, the velocity of the stream of the fuel-air mixture through the combustion chamber of a PVRD attains 100-120 m/sec. The stable combustion of the fuel-air mixture under these conditions encounters considerable difficulties.

Flame Stabilization and the Limits of Stable Fuel Combustion in VRD (Air-Reaction Engines)

The high flow velocities of the fuel-air mixture through the combustion chamber of a VRD can cause the separation of the flame thus

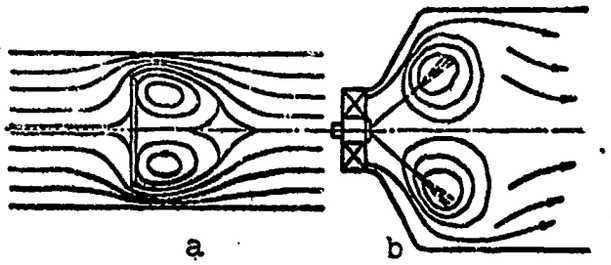


Fig. 47. Diagram of flame-front stabilization (anchoring) at great fuel-air-mixture flow velocities.
a) With a poorly streamlined body;
b) with a blade swirl chamber.

"extinguishing" the engine. To prevent the separation of the flame or to stabilize (anchor) the flame, special devices referred to as flame-holders can be installed within the combustion chamber.

A condition required for the stabilization of a flame in a VRD is the equality between the velocity of flame propagation and the velocity of the motion of the stream through the combustion chamber.

In VRD (air-reaction engines), as well as in other types of continuous-combustion engines, some portion of the fuel is consumed as a result of autoignition. As a result of the flow turbulence in these engines, individual volumes of the cold fuel-air mixture entering the flame are surrounded by gases heated to a temperature greater than autoignition temperature of the mixture. These volumes of mixture are burned up, on the one hand, as a result of the propagation of the flame over their surfaces, and on the other hand, as a result of autoignition after the heating of the mixture to a sufficiently high temperature. There seems to be some competition between the processes of flame propagation and the autoignition of the mixture. The greater the portion of fuel consumed as a result of the autoignition of the mixture, the higher the rate of mixture combustion within the engine.

It is clear that in order to increase the rate of fuel combustion

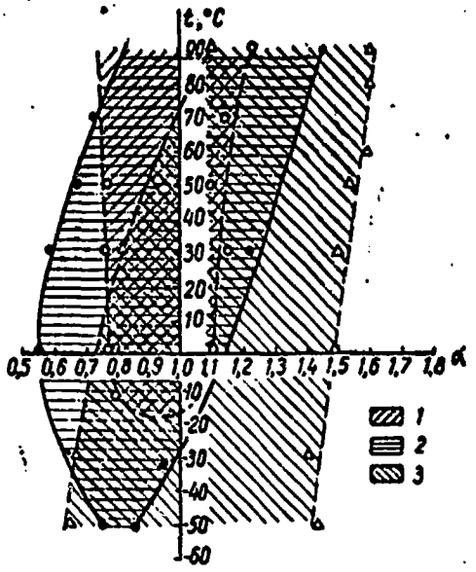


Fig. 48. Effect of chemical composition of fuel on limits of stable combustion under conditions simulating PVRD. Combustion limits: 1) Aromatic hydrocarbons; 2) naphthenic hydrocarbons; 3) n-paraffinic and olefinic hydrocarbons.

to limits which provide for stabilization of the flame, the portion of fuel that is consumed as a result of autoignition must be increased. Flame stabilization can be achieved by providing for hydrodynamic conditions within the engine under which the flame would receive a large quantity of individual large volumes of the fuel-air mixture. Such conditions can be provided by the positioning of poorly streamlined bodies in the way of the fuel-air mixture stream (Fig. 47). The eddies formed in back of the poorly streamlined bodies enhance the introduction of these individual volumes of the fuel-air mixture into the zone of high-temperature gases and promote intensive heat transfer within these volumes. Autoignition of the mixture volumes is a consequence of the foregoing, and this phenomenon takes place with great rapidity. A similar effect can be achieved by means of other flameholder designs; for example, use can be made of front units (fuel-nozzle ferrules) with blade swirl chambers, as used in TRD chambers.

Confirmation of the above-discussed concept with respect to the mechanism of flame stabilization by means of poorly streamlined bodies and other stabilizing (anchoring) devices is the pronounced relationship between the limits of stable combustion in VRD (air-reaction engines) (stabilization limits) and the chemical composition of the fuel. A similar pronounced effect, exerted by the chemical composition of the

fuel on the combustion process, is observed only in the case of fuel autoignition.

Figure 48 shows the investigational results that we obtained in studying the effect of the chemical composition of the fuel on the limits of stable combustion under conditions simulating those prevailing in ramjet VRD.

It follows from these data that at low fuel temperatures, the maximum limits of stable combustion are characteristic of the paraffinic hydrocarbons and the lowest limits are characteristic of the aromatic hydrocarbons. With an increase in the fuel temperature, the stabilization limits for aromatic hydrocarbons increase, whereas in the case of paraffinic and naphthenic hydrocarbons they diminish or remain constant. The limits of stable combustion are a characteristic of the fuel's ability to stabilize the flame. The wider the limits of stable combustion, the better the conditions for flame stabilization, the more reliable the operation of the engine in various regimes.

The data that we obtained indicate the great role played by fuel autoignition in the combustion process in VRD (air-reaction engines). Fuel autoignition not only determines combustion stability in the circulation zone, but it apparently also has an effect on the processes of complete fuel combustion. However, the role of autoignition in the complete-combustion zone during the combustion process is substantially less significant than it is in the circulation zone. This is associated with the reduced fresh-mixture concentration and reduced fresh-mixture turbulence intensity throughout the length of the combustion chamber.

Since fuel autoignition precedes the preflame oxidation which affects the velocity and nature of flame propagation in the case of autoignition, the conditions for the preflame preparation of the fuel in a VRD (air-reaction engine) also exert influence on the stabili-

zation of the flame.

In TRD (turbojet engines), the fuel is atomized and directed into the circulation zone. The preflame processes take place under conditions of moderate pressure and high temperatures close to the combustion temperature. Under these conditions, the basic preflame reactions take place in the vapor phase according to a mechanism which corresponds to the high-temperature stage of autoignition. Large drops of atomized fuel can also be oxidized in the liquid phase.

We can arrive at a conclusion as to the effect exerted by the conditions of preflame preparation of fuel on the limits of stable TRD (turbojet engine) operation on the basis of the results obtained in tests carried out on vaporization chambers in which the fuel is vaporized in special coils and enters the combustion chamber in vapor form. We know that vaporization chambers are characterized by substantially more narrow limits of stable combustion than chambers operating on atomized fuel. The reduction in the range of stable TRD (turbojet engine) operation in this case is a consequence, on the one hand, of the impairment of the conditions under which the preflame reactions take place as a result of the elimination of the liquid-phase fuel oxidation and, on the other hand, a result of the impairment of the conditions that are favorable for the formation of individual volumes of fuel which are consumed as a result of autoignition. It is of interest to point out that the limits of stable combustion expand in these same vaporization chambers during the preliminary vaporization of the fuel drops in an air atmosphere under conditions providing for the liquid-phase oxidation reactions.

In PVRD (ramjet engines), the fuel is atomized and directed into air heated by deceleration in the diffuser to a temperature whose magnitude is determined by the flight velocity. Under these conditions

comparatively intense fuel-drop oxidation is possible to the point at which the drops vaporize, and this in turn exerts an effect on autoignition of the fuel beyond the flameholder. The fuel film formed on surface of the flameholder as a result of the fuel drops striking the flameholder is subject to extremely intense liquid-phase oxidation in PVRD (ramjet engines). Fuel that has undergone preliminary oxidation ignites at a lower temperature. In this case, to heat an individual volume of the mixture in the circulation zone to the autoignition temperature requires less time. Consequently, a smaller volume will be consumed as a result of the propagation of the flame on the surface, and a greater volume will be consumed as a result of autoignition. A consequence of the above-described feature in the course of the preflame reactions in PVRD (ramjet engines) is, in particular, the greater sensitivity of an engine of this type to the quality of fuel, than is the case with TRD (turbojet engines).

Vibration Fuel Combustion in VRD (Air-Reaction Engines)

Under certain conditions of fuel combustion in VRD (air-reaction engines) the so-called vibration or pulsation (rigid) combustion takes place, this form of combustion characterized by the presence of periodic pressure pulsations (fluctuations) within the combustion chamber. Vibration combustion impairs engine economy and may result in the disruption of the functioning of the control equipment, as well as the buckling of the combustion chamber. As a result of vibration combustion the flame may become detached and the engine may be "extinguished." In the case of great pressure-oscillation amplitudes, mechanical damage may occur within the combustion chamber of the engine.

Vibration combustion occurs in VRD (air-reaction engines) before flame separation as the fuel-air mixtures are enriched or leaned, in the case of a substantial drop in the temperature of the fuel and air

entering the engine, and in the case of utilization of fuels exhibiting a high ignition lag.

The factors responsible for the occurrence of vibration combustion have not been adequately studied to the present time. In terms of its nature, vibration combustion is similar to predetonation combustion in a spark-ignition engine. This formal similarity in processes, as well as the above noted influence that the quality of the fuel has on the occurrence of vibration combustion, makes it possible to put forth the hypothesis which states that the factors responsible for the occurrence of detonation combustion in a spark-ignition engine are similar to those responsible for the occurrence of vibration combustion in VRD (air-reaction egines).

In both the first and the second type of engine, a portion of the fuel is consumed as a result of autoignition. In this case, because of the low pressure in the combustion chamber and because of the low temperature of the incoming fuel, the preflame reactions in the mixture volumes which are consumed as a result of autoignition take place under conditions corresponding to the low-temperature and transition autoignition zones. When the preflame reactions take place primarily in the transition zone, self-oscillatory chemical processes take place, and these result in the appearance of vibration combustion.

Consequently, in VRD (air-reaction engines), as well as in a spark-ignition engine, the preflame reactions taking place in the transition zone restrict the portion of fuel consumed as a result of autoignition, and an increase in this portion over a definite limit will result in the disruption of the normal combustion process.

Condition for the Most Economical Fuel Combustion in VRD (Air-Reaction Engines)

A characteristic of VRD (air-reaction engine) economy is the speci

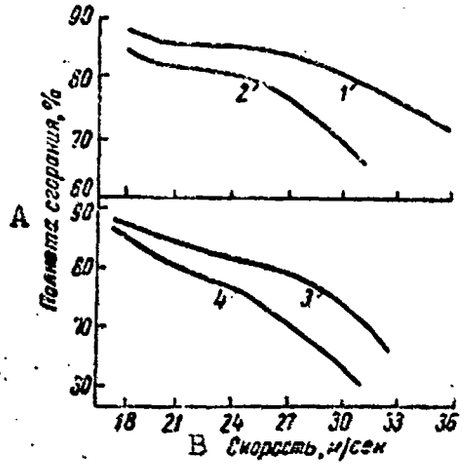


Fig. 49. Effect of fuel quality on coefficient of complete combustion in combustion chamber of TRD (turbojet engine). 1) n-Heptane; 2) isooctane; 3) n-hexane; 4) 2, 3-dimethylbutane; A) Completeness of combustion, %; B) speed, m/sec.

fic fuel consumption or the specific thrust of the engine. The specific fuel consumption $G_{ud}$ – the hourly fuel flow rate per 1 kg of thrust developed by the engine – is equal to

$$G_{ud} = (G_t/R)\ 3600 \text{ kg per kg of thrust, per hour.}$$

The thrust R developed by the engine with a fuel flow rate $G_t$ is a function of a number of parameters. The parameter which characterizes the efficiency of the combustion process is the coefficient of fuel-combustion completeness $\varphi_{sg}$ which is determined by the ratio of the increment in heat content (enthalpy) of the products of combustion to the heat of combustion of the fuel entering the combustion chamber.

It was pointed out above that the efficiency of the combustion process in VRD (air-reaction engines) is to a great extent determined by the relationship between the portion of the fuel consumed as a result of autoignition and that portion of the fuel which is consumed as a result of the propagation of the flame along the surface of the mixture. The greater the quantity of fuel consumed as a result of autoignition, the more effective (efficient) the combustion. That portion of the fuel consumed as a result of autoignition is determined primarily by the structural features of the chamber, the manner in which the preflame preparation of the fuel-air mixture is carried out, the degree of stream turbulence behind the stabilizer (flameholder), etc. It is clear therefore that in an efficiently designed combustion chamber, high values for the coefficient of combustion completeness can usually be

TABLE 22

Fuel Characteristics

| 1 Топливо | 2 Температура кипения, °С | 3 Нормальная скорость распространения пламени, см/сек | 4 Температура воспламенения, °С |
|---|---|---|---|
| 5 *н*-Гептан . . . . . | 98,4 | 38,6 | 247 |
| 6 Изооктан . . . . . | 99,3 | 34,6 | 447 |
| 7 *н*-Гексан . . . . . | 69,0 | 38,5 | 261 |
| 8 2,3-диметилбутан . . | 58,0 | 36,3 | 421 |

1) Fuel; 2) boiling point, °C; 3) normal speed of flame propagation, cm/sec; 4) ignition temperature, °C; 5) n-heptane; 6) isooctane; 7) n-hexane; 8) 2, 3-dimethylbutane.

attained.

Unlike the combustion of fuels in contemporary spark-ignition engines, in VRD (air-reaction engines) structural measures can be employed in order to achieve high-economy combustion on any fuel quality. However, this circumstance does not indicate any lack of influence on the part of fuel quality on the combustion process in VRD (air-reaction engines). In an engine of this type, as well as in all cases in which a substantial portion of the fuel is consumed as a result of autoignition, the molecular structure of the fuel affects combustion. Evidently, a fuel characterized by a shorter autoignition lag, all other conditions being equal, and by a lower autoignition temperature, will burn up in a VRD (air,reaction engine) with a high coefficient of combustion completeness. Confirmation of this statement is given, for example, by the data presented in Fig. 49 and in Table 22 [31].

We can see from Table 22 and Fig. 49 that fuels that are virtually identical in terms of physical properties and the normal speed of flame propagation, but differing in terms of autoignition temperature, burn up with various coefficients of combustion completeness. The lower the autoignition temperature, the higher the coefficient of combustion com-

pleteness. The data presented above again indicate the significant role played by autoignition in the fuel-combustion process in a VRD. Moreover, it follows from these data that in those cases in which the structural possibilities of high-economy fuel combustion in a VRD (air-reaction engine) are fully utilized, an additional effect can be achieved by using fuels exhibiting a small autoignition lag and low autoignition temperature.

FUEL COMBUSTION IN A LIQUID-FUEL ROCKET ENGINE (ZhRD)

Rocket engines, unlike VRD (air-reaction engines) use an oxidizer carried on board the flying craft for purposes of burning (causing the combustion) of the fuel (combustible). A ZhRD (liquid-fuel rocket engine) is a continuous-combustion engine in which the thrust is produced as a result of the reaction of a gas stream formed in the combustion of a mixture of liquid fuel (combustible) with liquid oxidizer.

The idea for the development of a ZhRD belongs to K.E. Tsiolkovskiy. In 1903, in the journal "Scientific Review" his work "The Investigation of Outer Space by means of Reaction Devices" was published, and here he outlined his theory of rocket flight and provided the scientific basis for the possibility of using liquid rocket engines for flight in interplanetary space.

Figure 50 shows a diagram of one of Tsiolkovskiy's liquid rocket engines in which he uses liquid hydrocarbons and liquid oxygen as the fuel. In addition to the development of the basic ZhRD design, K.E. Tsiolkovskiy resolved a number of structural problems. Many of his suggestions have been incorporated in contemporary ZhRD (liquid rocket engines). For example, the cooling of the combustion chamber by means of the combustible, the installation of the rocket control surfaces (gas vanes) in the stream of the exhaust gases, etc.

The utilization of liquid oxygen or some other active oxidizer

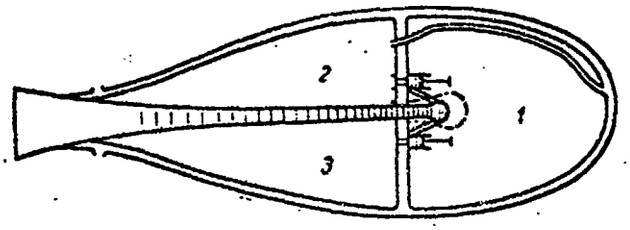


Fig. 50. Diagram of liquid rocket engine, after K.E. Tsiolkovskiy. 1) Crew, breathing equipment; 2) liquid freely evaporating oxygen at extremely low temperature; 3) liquid hydrocarbon.

rather than the oxygen of the air as the oxidizer makes it possible substantially to increase the heating value of the fuel, i.e., the quantity of heat referred to 1 kg of the products of combustion. In this case, the heat is not expended on the heating of ballast components in the oxidizer, e.g., such as the nitrogen in the air. As a result, in a ZhRD (liquid fuel rocket engine) the products of combustion are heated to extremely high temperatures (3000-4000° K), and this makes it possible to attain high exhaust velocities for the products of combustion and, consequently, greater power than is attainable with any other types of engines. For example, the German V-2 rocket developed a power in excess of 600,000 hp.

The basic diagram of a contemporary ZhRD (liquid rocket engine) is shown in Fig. 51. The liquid oxidizer and the liquid fuel (combustible) is supplied to the injectors by means of pumps set into motion by an auxiliary turbine, and the spray nozzles (injectors) are mounted in the head of the engine. The spray nozzles (injectors) are positioned in the engine head so as to provide for the best mixing of the fuel components. The fuels may be hypergolic when the combustible comes into contact with the oxidizer, or the fuels may be nonhypergolic. The latter are ignited by means of special devices. Most frequently they are igni-

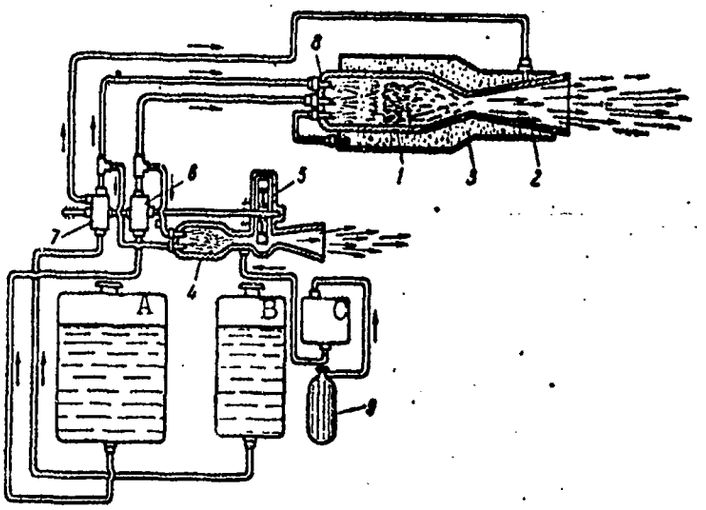


Fig. 51. Diagram of ZhRD (liquid fuel rocket engine) with turbopump fuel-feed system. 1) Combustion chamber; 2) reaction nozzle; 3) fuel (combustible) cooling jacket; 4) auxiliary-engine combustion chamber; 5) auxiliary vapor-gas turbine; 6, 7) pumps set into motion by the auxiliary turbine and feeding the ZhRD combustion chamber with fuel (combustible) and oxidizer; 8) spray nozzles (injectors); 9) compressed-air flask for supply of water to cool the combustion chamber of the auxiliary turbine. A) Oxidizer; B) fuel (combustible); C) water.

ted by means of an ignition flame formed as a result of the utilization of a hypergolic initiating fuel.

Ignition may also be achieved by means of a special "pyrotechnic" device. The latter may consist of one or more powder cartridges which are ignited by means of electricity. A powder cartridge of this type burns for several seconds and will ignite the mixture.

After the ignition of the fuel in the combustion chamber, continuous combustion of the incoming fuel is established. The kinetic energy of the products of combustion is converted into engine thrust in the nozzle assembly.

The structural design of an engine is determined by its designation. The diagram of the ZhRD with turbopump fuel feed considered in Fig. 51 is used generally for engines intended for extensive operation. For short-operation engines (booster engines, antiaircraft missiles) the small fuel-tank capacity makes it possible to use the gas-flask method of fuel feed (Fig. 52).

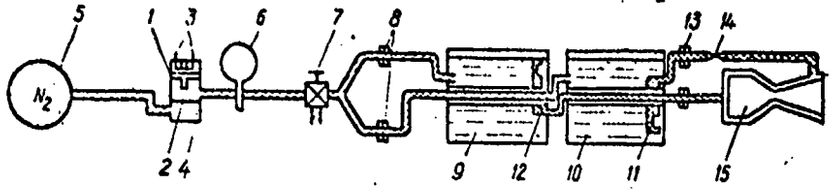


Fig. 52. Schematic diagram of ZhRD (liquid rocket engine) with gas-flask (pressure tank) pressurized-propellant feed system (the Wasserfall antiaircraft missile). 1) Piston set into motion during combustion of powder charge; 2) burst diaphragm; 3) 24 v voltage; 4) start valve; 5) pressurizing-gas (nitrogen) container (flask) under a pressure of 250 atm; 6) pressure regulator; 7) check valve; 8) two burst diaphragms set for a pressure of 10 atm; 9) fuel (combustible) tank; 10) oxidizer tank; 11) flexible tubing with weights at one end; 12) hinged connection of intake connection tube; 13) two burst diaphragms set for a pressure of 20 atm; 14) calibrated jet nozzles; 15) combustion chamber of engine (pressure in chamber, 19 atm).

The designation of the engine also determines the requirements imposed on the thrust developed by the engine and on the duration of engine operation, and this has an effect on the dimensions of the combustion chamber, the capacity of the fuel (propellant) tank, and on the selection of the fuel (propellant) components.

Features of the Combustion Process in ZhRD (Liquid Rocket Engines)

Unlike other continuous-combustion engines, the fuel (propellant) combustion process in ZhRD (liquid rocket engines) takes place at extremely high temperatures (3000-4000° K) and pressures (up to 100 atm). Under these conditions, the chemical reactions of interaction betwee-

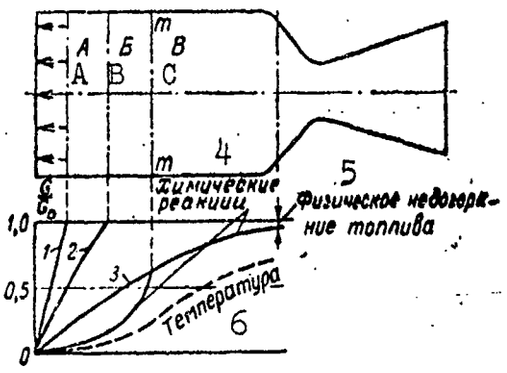


Fig. 53. Zones in which the primary processes take place within the combustion chamber of a ZhRD (liquid rocket engine) [33]. A) Zone of fuel (propellant) atomization; B) vaporization zone; C) mixing zone and zone of chemical reactions; m - m) section of transition of combustion from kinetic region to diffusion region; $G/G_0$) portion of fuel (propellant) referred to per-second flow rate. 1) Atomization; 2) vaporization; 3) mixing; 4) chemical reaction; 5) physical incomplete combustion of fuel (propellant); 6) temperature.

the fuel (combustible) and the oxidizer take place at an extremely fast rate. The time that the fuel (propellant) stays in the combustion chamber (from the instant at which it enters to the instant at which the products of combustion are formed) is calculated at 0.003-0.008 sec. At the same time, just as in a VRD (air-reaction engine), the combustion process takes place in an extremely turbulent stream of combustible and oxidizer vapors. Near the engine head there are intensive countercurrents of products of combustion. All of this makes it possible to consider the combustion process in a ZhRD (liquid rocket engine), as in the case of a VRD (air-reaction engine), as consisting of two simultaneous processes – the propagation of the flame and the autoignition of the mixture volumes of combustible and oxidizer vapors as these enter the high-temperature zone.

The combustion chamber of a ZhRD (liquid rocket engine) is conventionally divided into several characteristic zones (Fig. 53). The first zone is the propellant atomization zone and is situated in the immediate vicinity of the engine head. The streams of combustible and oxidizer coming out of the injectors are atomized into drops primarily in this zone. The following zone is the vaporization zone in which the propellant components are mixed. This zone is characterized by intensive vaporization processes involving the propellant drops and the mixing of

oxidizer and combustible vapors. It is in this zone that the intensive liquid-phase combustible-drop oxidation processes take place with both liquid and gaseous oxidizers, the latter generally being present in a volume several times in excess of the quantity of combustible. At the same time the combustible and oxidizer vapors begin to enter into the reaction. Then follows the mixing zone and the zone of chemical reactions. This zone can be divided into two regions -- the region of kinetic combustion and the region of diffusion combustion. In the kinetic reaction region the propagation of the flame takes place at a relatively low velocity. A substantial portion of the entire propellant consumed in this region burns up as a result of the autoignition of the volumes of the gaseous combustible and oxidizer mixture, with these volumes flushed by the countercurrents of the products of combustion. Although the mixture undergoes autoignition virtually instantaneously, the entire autoignition process, including the preflame preparation of the mixture, takes place rather slowly. The periodic preflame reactions similar to the reactions (considered above) taking place in the transition autoignition zone take place in this region. The rate of propellant combustion in the kinetic region is limited not so much by the mixing processes but by the kinetics of the chemical reactions, and this determined the designation of this region.

The region of diffusion combustion is characterized by high gas temperature. Here, the rate of the chemical reaction is substantially in excess of the rate of mutual diffusion between the molecules of the combustible and those of the oxidizer, as well as the rate of component mixing. In this region, the combustion of the fuel takes place primarily as a result of the propagation of the flame in the unconsumed mixture. Autoignition processes play an insignificant role in this region.

The examined subdivision of the combustion chamber of ZhRD (liquid

rocket engines) is conditional, since it is not possible to define clear boundaries between zones in the engine. Nevertheless, this subdivision is useful, since it makes it possible to conceptualize the processes taking place within the combustion chamber of a ZhRD (liquid rocket engine).

Unstable Combustion in a ZhRD (Liquid Rocket Engine)

Unstable or vibration combustion in ZhRD (liquid rocket engines) (hard combustion) takes place in all types of ZhRD regardless of the dimensions and configurations of the combustion chambers, and also independent of the propellant and feed systems used.

Unstable combustion appears in the form of periodic pressure fluctuations in the combustion chamber. When the amplitude of the oscillation (fluctuation) is not great and there is no disruption of the normal operation and utilization of the engine, the combustion is conditionally regarded to be stable.

A thoroughly refined theory of unstable combustion in ZhRD does not yet exist. Experimenters have distinguished two types of pressure oscillations which can occur in the combustion chamber of a ZhRD - high-frequency (above 1000 cps) and low-frequency (below 300 cps). We know of the following concepts which serve to explain the physical mechanism responsible for the appearance of oscillations (fluctuations) within a ZhRD chamber.

Low-frequency instability is a result of the interaction of the oscillations within the combustion chamber with those oscillations within the feed system of the engine. With a change in the pressure within the combustion chamber, given constant pressure in the feed system, there is a change in the fuel (propellant) - feed regime. For example, with an increase in pressure in the combustion chamber, the quantity of fuel fed to the engine is reduced. A reduction in the quantity

of fuel fed to the engine in turn reduces the pressure within the combustion chamber. The combustion of the incoming fuel (propellant) takes place in the engine, but not instantaneously; rather it takes place over a certain interval of time that is a function of the time required to convert the fuel (propellant) into the products of combustion. During this time, the pressure continues at its elevated level, and the fuel (propellant) flow rate remains at its reduced level. Then the process is repeated in reverse. Because of the reduced pressure in the combustion chamber, the quantity of fuel (propellant) fed into the engine is increased, and this increases the pressure within the combustion chamber. In this case, as a result of the fact that there now is time for the conversion to take place, the elevated pressure lasts longer in the combustion chamber than is required for the equalization of the pressure, and the oscillations are not damped. These oscillations are characterized by low frequencies as a result of the inertia of the mass of liquid propellant subjected to these oscillations.

Experimental investigations of the phenomenon of low-frequency instability confirm the physical mechanism of its origin as presented above. For example, low-frequency instability is reduced by limiting the conversion time, by increasing the pressure difference between the tank and the chamber, by increasing the volume of the combustion chamber and the length of the fuel manifold, and by reducing the lateral cross section of the fuel manifold or by increasing the mass rate therein [33].

High-frequency instability of combustion in combustion chambers of ZhRD is characterized by regular oscillations having a frequency ranging from 1000 to 12000 cps. The amplitude of the oscillation varies within a range of tenths of a fraction of an atmosphere to 100% of the pressure within the chamber. Longitudinal high-frequency oscillations of

of various types have been experimentally observed, including oscillations of the shock and sinusiodal types [34]. Generally, in the case of developed high-frequency instability, we note the appearance of shock waves that are propagated along the combustion chamber. Evidently, these high-frequency oscillations are associated with the features encountered in the combustion process within ZhRD (liquid rocket engines).

At the present time there is no generally accepted standpoint for the physicochemical model of this phenomenon. Taking into consideration the above-considered features encountered in the combustion process in ZhRD, it becomes possible to explain this phenomenon in terms of the concepts which we employed to explain detonation combustion in a spark-ignition engine.

We pointed out above that in the kinetic region of the combustion chamber of a ZhRD, a substantial portion of the fuel (propellant) is burned as a result of the autoignition of the turbulent fresh-mixture volumes.

Under conditions of high pressure within the combustion chamber of a ZhRD, despite the rather high temperatures, high-reaction-capacity molecules of the combustible and oxidizer may interact on the basis of the mechanism for the transition stage of autoignition. In this case, in the volumes of the combustible and oxidizer mixture periodic reactions take place and accordingly there is a periodic liberation of heat within the gas, resulting in the occurrence of compression waves.

In the kinetic region of the combustion chamber of a ZhRD (liquid rocket engine) it is possible to provide for the second condition which results in the formation of undamped shock waves from the compression waves that are produced: the quantity of matter reacting in each subsequent instant of time can be greater than the preceding quantity.

In fact, under conditions of relatively moderate temperatures within the kinetic region, the liberation of heat in the wave results in the progressive heating up of the adjacent layers of the mixture and the self-acceleration of the waves to values of the velocity $W_x$ at which the liberation of heat in the wave in each subsequent instant becomes equal to the quantity of heat liberated at the preceding instant of time.

Evidently, high-frequency instability of combustion is a function both of the thermodynamic and hydrodynamic conditions within the combustion chamber of the ZhRD (liquid rocket engine). The hydrodynamic conditions determine, in particular, the number and volume of the autoignition foci. An increase in the number and volume results in an increase in the amplitude of the oscillation. The hydrodynamic conditions in turn are functions of the geometry of the combustion chamber. This can, apparently, be explained by the effect that the length of the combustion chamber, as well as the shape and the length of the converging part of the nozzle [35-37], exert on the occurrence and intensity of high-frequency instability. We should also anticipate a rise in high-frequency instability with an increase in the pressure within the combustion chamber, since in this case the temperature range expands, i.e, the range within which the periodic preflame processes take place.

The increase in the intensity of the high-frequency instability of combustion that takes place as a result of an increase in pressure was established experimentally in References [34-36]. As can be seen, this concept of the physicochemical conditions for the occurrence of unstable combustion makes it possible qualitatively to explain certain experimental data. It should be pointed out that Yu.Kh. Shaulov and M.O. Lerner [37] pointed both to the periodic processes in the chemical kinetics as well as to one of the possible factors responsible for

the occurrence of unstable combustion in ZhRD (liquid rocket engines).

High-frequency instability of combustion in ZhRD, unlike low-frequency combustion instability, is apparently not associated with the feed system of the engine. At the same time, both disruptions of the normal combustion process may be closely associated with one another. For example, high-frequency instability may serve as the initial factor responsible for the occurrence of low-frequency instability, and the latter may serve to intensify high-frequency instability.

The Influence that the Combustion Process Exerts on ZhRD Economy

The magnitude of specific thrust for any continuous-combustion engine is determined by the heating value of the fuel (propellant) employed, and here we must take into consideration the possible dissociation of the products of combustion and the coefficient of combustion completeness. High-reaction-capacity propellant components used in ZhRD are generally characterized by high values of the coefficient of combustion completeness. A reduction in the coefficient of combustion completeness is observed when the normal combustion process is disrupted. For example, the appearance of low-frequency combustion instability results in a reduction of specific engine thrust.

The intensity of unstable combustion in ZhRD (liquid rocket engines) is associated with the relationship between the quantity of fuel consumed as a result of autoignition and the quantity of fuel that is consumed as a result of the propagation of the flame along the surface of the gas mixture. Unlike VRD (air-reaction engines) an increase in this relationship (ratio) sometimes results in a reduction of engine economy as a result of the appearance of unstable combustion with great oscillation amplitudes.

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[Footnotes]

147 For additional details, see the special references, e.g., [8, 9].

166 According to the standpoint of G.S. Shimonayev.

## Chapter 7

## HEAT OF COMBUSTION OF HYDROCARBON FUELS

### METHODS OF COMPUTING HEAT OF COMBUSTION

In addition to the standard methods for determining heat of combustion (see Chapter III), various empirical formulas are employed for planning and design purposes; these can indicate the heat of combustion of the fuel with a lower accuracy but by a simpler route than the bomb determination.

The error of a heat-of-combustion calculation made by the empirical formulas is $\pm$ 2 to 3%.

Basic to the empirical working formulas proposed by various authors are the following:

1) the elementary composition of the fuel;

2) the quantity of air (oxygen) required to burn the fuel;

3) the heat of formation of the fuel;

4) the physicochemical characteristics of the fuel.

In the first case, we depart from the fact that the fuel's heat of combustion is equivalent to the sum of the heats of combustion of the individual elements forming the fuel. Many formulas are based on this.

The author of one of the first formulas, and one which has practical importance at the present time, was the great Russian scientist D.I. Mendeleyev.

However, combustion of a fuel takes place in a more complex manner than does combustion of the individual elements forming the fuel to the

final conversion products.

In this case, we disregard the possibility of formation of various intermediate compounds with absorption or liberation of heat.

As an example, we present the formula [1]

$$Q^{n} = 7847C + 28670\left(H - \frac{O}{8}\right) + 2500\,S - 595W, \qquad (1)$$

where $Q^{n}$ is the lower-limit heat of formation in kcal/kg, C is the fractional content of carbon in the fuel, H is the fractional content of hydrogen in the fuel, O is the fractional content of oxygen in the fuel, S is the fractional content of sulphur in the fuel and W is the fractional content of water in the fuel.

In the second case, the quantity of oxygen necessary for complete combustion of the elements composing the fuel is used as the basis for the empirical formulas.

As an example, we present the formula [2]

$$Q^{n} = \left[8910 - 620\frac{C}{1-(a+W)}\right]C + 21735\left(H - \frac{O}{8{,}05}\right) + 2500S - 585W, \qquad (2)$$

where a is the fractional content of ash in the fuel and 585 is the heat of combustion of water expressed in kcal/kg.

The remaining symbols have the same significance as for Formula (1).

A somewhat higher accuracy in the calculations (± 2%) is given by the possibility of deriving the formula [3]

$$Q^{n} = 8400C + 22500H + 1500N + 2500S - 2650O - 585W, \qquad (3)$$

where N is the fractional content of nitrogen in the fuel.

The remaining symbols have the same significance as in Formula (1).

In writing Formulas (2) and (3), the elementary composition of the fuel was again used as the point of departure; as has already been noted, this is the source of the inadequate accuracy delivered by the calculations.

The heat of combustion of a liquid fuel may be computed with an accuracy approaching that of calorimetric determination by the formula of D.P. Konovalov [4]:

$$Q^{н} = 3050K, \tag{4}$$

where K is the quantity of oxygen necessary to burn a unit weight of the fuel.

The quantity K is computed by the formula

$$K = \frac{\frac{8}{3}C + 8H - O}{100}, \tag{5}$$

where C, H and O are the contents of carbon, hydrogen and oxygen in the fuel, respectively, expressed in %.

According to this formula, the quantity of heat liberated in combustion of the fuel, referred to a unit weight of oxygen consumed, differs by no more than 1 – 2% for all fuels.

In the third case, the empirical formulas are based on the familiar Hess law, from which it follows that the heat of combustion of a fuel corresponds to the difference between the heats of formation of the compound being burned and the sum of the heats of formation of its ultimate combustion products (water, carbon dioxide, etc.).

Finally, in the fourth case, for liquid hydrocarbon fuels, which consist basically of two elements – carbon and hydrogen – a definite relationship has been established between the proportions of these elements, their boiling point, aniline point, density [5], hydrocarbon structure [6] and other indices that characterize the hydrocarbon fuel on the one hand, and the heat of combustion on the other.

Table 23 [7] shows the relationship between the carbon-to-hydrogen ratio and heat of combustion for a hydrocarbon fuel of this composition.

Knowing the chemical composition of a liquid fuel, we may compute its heat of combustion by the following formula [6] with an accuracy

TABLE 23

Lower-Limit Heat of Formation of Liquid Petroleum Products at 15.5° and Constant Pressure (in kcal/kg) [9]

| 1 Элементарный состав топлива (отношение углерод/водород) | 2 Углеводородные топлива | 3 Индивидуальные углеводороды |
|---|---|---|
| 6,0 | 10 360 | 10 360 |
| 6,4 | 10 240 | 10 250 |
| 6,8 | 10 120 | 10 150 |
| 7,2 | 10 010 | 10 070 |
| 7,6 | 9 925 | 10 000 |
| 8,0 | 9 820 | 9 930 |
| 8,4 | 9 730 | 9 875 |
| 8,8 | 9 650 | 9 830 |
| 9,2 | 9 580 | 9 780 |
| 9,6 | 9 520 | 9 760 |
| 10,0 | 9 470 | 9 740 |

1) Elementary composition of fuel (carbon/hydrogen ratio); 2) hydrocarbon fuels; 3) individual hydrocarbons.

within 1 to 2%:

$$Q^{v} = 104{,}2\,n_{C} + 26{,}05\,n_{H} + 13{,}0\,n_{1} + 46{,}1\,n_{2} + 6{,}5\,n_{3} - 3{,}5\,n_{ar-al} - 6{,}5\,n_{ar-ar} \qquad (6)$$

where $Q^{v}$ is the upper-limit heat of combustion in kcal/mole at 20°, $n_C$ is the number of carbon atoms in the molecule, $n_H$ is the number of hydrogen atoms in the molecule, $n_1$ is the number of double bonds in the olefin molecule or in the side chains in the case of ring compounds, $n_2$ is the number of triple bonds in the molecules of acetylene hydrocarbons, $n_3$ is the number of double bonds in the ring for unsaturated naphthenes, $n_{ar-al}$ is the number of bonds between the aromatic ring and the alkyl groups, $n_{ar-ar}$ is the number of bonds between aromatic rings.

In computing the heat of combustion for polycyclic aromatic hydrocarbons, $n_{ar-ar}$ is equal to the number of aromatic rings in the pol

cyclic grouping minus one multiplied by two. For example, $n_{ar-ar}$ assumes the values

| | |
|---|---|
| for diphenyl | 1 |
| " triphenylbenzene | 3 |
| " naphthalene | 2 |
| " phenanthrene | 4 |
| " chrysene | 6 |
| etc. | |

HEAT OF COMBUSTION AS A FUNCTION OF THE CHEMICAL NATURE OF FUELS

The heat of combustion of a fuel depends on two factors:

1) on the quantity of combustible compounds in the fuel; this applies principally to solid fuels whose composition includes ash and a considerable quantity of moisture;

2) on the chemical composition of the fuel or on the proportions of the elements composing the combustible part of the fuel and, consequently, on the chemical composition of hydrocarbon liquid fuels.

Table 24 lists heats of combustion for the combustible parts of various fuels and the elements composing them.

In practice, a liquid hydrocarbon fuel consisting almost entirely of compounds whose structures incorporate carbon and hydrogen has the highest heat of combustion. The unit-weight heat of combustion of hydrogen is 3.5 times that of carbon. For this reason, the higher the hydrogen content, the higher will be the heat of combustion of a hydrocarbon fuel.

For paraffinic hydrocarbons, carbon content varies insignificantly - in the range from 84 to 85%; for naphthenic hydrocarbons, this quantity is constant at approximately 85.75%, and for aromatic hydrocarbons it varies over a wide range from 91 to 87.5%, depending upon the length of the side chains.

The unit-weight heats of combustion of fuels vary in the same sequence as carbon content: negligibly for paraffinic and naphthenic

hydrocarbons and up to 500 kcal (Fig. 54) for aromatic hydrocarbons with 6 to 20 carbon atoms.

TABLE 24

Lower-Limit Heats of Combustion of Fuels Referred to Burning Mass (in kcal/kg)

| 1 Топливо | 2 $Q^н$, ккал/кг |
|---|---|
| 3 Газообразные соединения | |
| 4 Водород; сгорает в воду | 28 557 |
| 5 Окись углерода; сгорает в углекислый газ | 2 429 * |
| 6 Метан | 11 970 |
| 7 Этилен | 11 145 |
| 8 Ацетилен | 11 499 |
| 9 Твердое топливо | |
| 10 Углерод; сгорает в углекислый газ | 8 100 * |
| 11 Углерод; сгорает в окись углерода | 2 433 |
| 12 Антрацит | 8500—9000 |
| 13 Каменный уголь | 7000—8000 |
| 14 Бурый уголь | 6000—7000 |
| 15 Торф | 5000—6000 |
| 16 Дерево | 4 500 |
| 17 Жидкое топливо [8] | |
| 18 Нефть | 10 500 |
| 19 Авиационный бензин, сорт 100/130 | 10 530 |
| 20 Бензин автомобильный (средний) | 10 486 |
| 21 Дизельное топливо, парафинистое | 10 386 |

*For carbon and carbon monoxide, in which there is no hydrogen and water does not form on combustion, the concept of lower-limit heat of combustion is not applicable. Their full heats of combustion are listed.

1) Fuel; 2) $Q^н$, kcal/kg; 3) gaseous compounds; 4) hydrogen; burns to water; 5) carbon monoxide; burns to carbon dioxide; 6) methane; 7) ethylene; 8) acetylene; 9) solid fuel; 10) carbon; burns to carbon dioxide; 11) carbon; burns to carbon monoxide; 12) anthracite; 13) coal; 14) lignite; 15) peat; 16) wood; 17) liquid fuel [8]; 18) petroleum; 19) aviation gasoline, grade 100/130; 20) automobile gasoline (medium); 21) diesel fuel, paraffinic.

The unit-volume heat of combustion of hydrocarbons is determined not only by the unit-weight heat of combustion, but also by density, which varies as a function of the hydrocarbon's structure.

For hydrocarbons fuels that boil out in the range from 80 to 300°, the density $\rho_4^{20}$ varies as follows [9, 11, 12].

| | |
|---|---|
| For paraffinic hydrocarbons . . . . | from 0.68 to 0.80 |
| For naphthenic hydrocarbons . . . . | " 0.74 " 0.84 |
| For monocyclic aromatic carbons . . . . . | " 0.86 " 0.90 |
| For bicyclic hydrocarbons . . . . . | " 0.92 " 1.04 |

As we see, even within a single class of hydrocarbons, density varies significantly; this is determined not only by the molecular weight of the hydrocarbons, but also by the structure of the isomers.

Among the paraffinic hydrocarbons, those with three and more methyl groups in the molecule and located on the same carbon atom or in a row show the highest densities. Paraffinic hydrocarbons having branched or, as they are sometimes called, comb structures are characterized by high densities. Here, the number of side chains must be as large as possible, their arrangement as compact as possible; the chain length may be restricted to only one methyl group.

Thus, for example, the density of n-dodecane ($C_{12}H_{26}$) is 0.7487, while that of 2,2,3,4,5,5-hexamethylhexane ($C_{12}H_{26}$) is 0.7925.

We observe the same relationship for naphthenic hydrocarbons as for paraffinic hydrocarbons. As the number of side chains increases and as they are placed more compactly in the molecule, density rises markedly. Thus, for example, a naphthenic ring with side chains in the ortho position have densities from 0.795 to 0.815 for $C_8 - C_{12}$ hydrocarbons, in contrast to hydrocarbons whose side chains occur in the meta position, which have densities of 0.785 to 0.800. Naphthenic hydro-

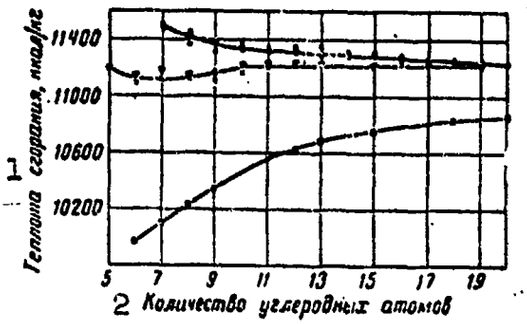


Fig. 54. Upper-limit unit-weight heat of combustion of hydrocarbons as a function of their structure [10]. O) Paraffinic hydrocarbons of normal and isomeric structure; ∇) derivatives of cyclohexane with normal-structured side chain; X) cyclopentane derivatives with normal-structured side chain; □) benzene ring with normal-structured side chain. 1) Heat of combustion, kcal/kg; 2) number of carbon atoms.

carbons are characterized by a density increasing sharply as the number of methyl groups in the 1, 2, 3, 4, 5, and 6 positions.

Like the paraffinic and naphthenic hydrocarbons, monocyclic aromatic compounds have higher densities as the number of side chains compactly arranged on the benzene ring increases. Thus, hydrocarbons with side chains in the ortho position have densities higher than those of hydrocarbons with the same molecular weight but with side chains located in the para and meta positions. Density increases with increasing number of side chains on neighboring carbon atoms in the benzene ring.

Bicyclic compounds are distinguished by the highest densities.

The densities of hydrocarbons of all classes increase with increasing number of short side chains (methyl groups) situated in the molecule as symmetrically and compactly as possible as compared with the densities of the corresponding hydrocarbons having the same molecular weights and empirical formulas but different structures.

Obviously, a fuel with a higher density and, consequently, a higher unit-volume heat of combustion (Fig. 55) can be obtained by forming mixtures of hydrocarbons of a definite chemical structure.

Hydrocarbons having different structures are present in petroleum and in products of refinement of petroleum raw materials. Industrial techniques for separating the hydrocarbons and extracting them on the

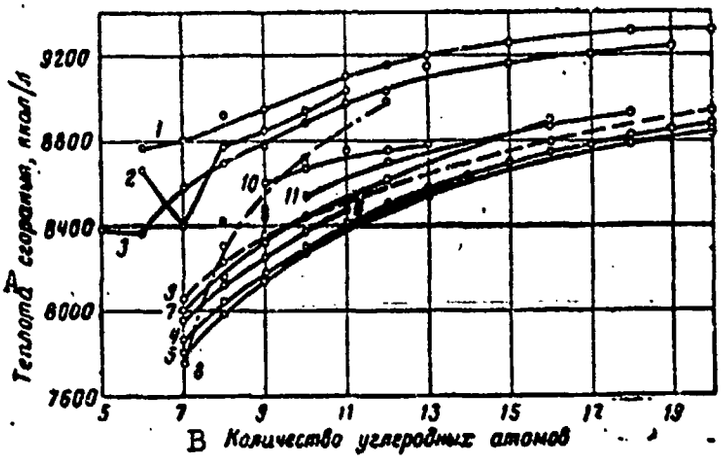


Fig. 55. Relationship between upper-limit unit-volume heat of combustion of hydrocarbons and number of carbon atoms in the molecule [12]. 1) Benzene ring with normal-structured side chain; 2) cyclohexane with normal-structured chain; 3) cyclopentane with normal-structured chain; 4) normal-structured paraffinic hydrocarbons; 5) paraffinic hydrocarbons with single methyl side group; 6) paraffinic hydrocarbons with two methyl side groups at the same C atom; 7) paraffinic hydrocarbons with two methyl side groups on adjacent carbon atoms; 8) paraffinic hydrocarbons with three or more methyl groups on adjacent carbon atoms (compact arrangement); 9) paraffinic hydrocarbons with single ethyl groups; 10) paraffinic hydrocarbons with two ethyl groups on the same C atom; 11) paraffinic hydrocarbons with two ethyl groups on different C atoms. A) Heat of combustion, kcal/liter; B) number of carbon atoms.

basis of their structures are not adequately developed. The possibilities offered in this respect are quite considerable.

The data listed in Table 25 provide some conception of the heats of combustion of hydrocarbon fractions obtained from various raw materials and by various refining methods.

As will be seen from the data in Table 25, the difference between the maximum and minimum values of the heats of combustion for the fractions listed, which are of the same chemical structural type, lie be-

TABLE 25

Limits of variation of lower-limit heat of combustion $Q^n$ of hydrocarbon mixtures (in kcal) [10]

| 1 Пределы выкипания углеводородных фракций, °С | 2 Моноциклические ароматические углеводороды | | 3 Нафтеновые углеводороды | | 4 Парафиновые углеводороды | |
|---|---|---|---|---|---|---|
| | 5 на кг | 6 на л | 5 на кг | 6 на л | 5 на кг | 6 на л |
| 100—150 | 9950—9850 | 8450—8200 | 10350—10200 | 8500—7400 | 10770—10490 | 7950—7730 |
| 150—200 | 10020—9670 | 8920—8300 | 10440—10130 | 8600—7600 | 10720—10510 | 8170—7630 |
| 200—250 | 9950—9820 | 9100—8600 | 10400—10100 | 8680—7700 | 10680—10430 | 8350—8070 |
| 250—300 | 9970—9770 | 9350—8670 | 10350—10100 | 8850—7850 | 10470—10300 | 8270—8240 |
| 300—350 | 9980—9950 | 9170—8770 | 10250—10100 | 8800—8100 | 10420—10350 | 8420—8250 |

1) Boiling range of hydrocarbon fractions, °C; 2) monocyclic aromatic hydrocarbons; 3) naphthenic hydrocarbons; 4) paraffinic hydrocarbons; 5) per kg; 6) per liter.

tween 30 and 350 kcal/kg for the unit-weight heat of combustion and between 30 and 1100 kcal/liter for the unit-volume heat. The difference between the unit-volume heats of combustion for naphthenic hydrocarbons is particularly large (700 to 1100 kcal/liter).

This last fact indicates that a considerable increase in the unit-volume heat of combustion of the fuel as a whole can be achieved by introducing certain industrial mixtures of naphthenic hydrocarbons into the fuel.

## SIGNIFICANCE OF FUEL HEAT OF COMBUSTION FOR ENGINES

During the time when engines requiring high-yield liquid fuels were rapidly making their appearance, the importance of the fuel's heat of combustion and the necessity of increasing it further increased sharply.

The difficulty of achieving further increases in the heats of combustion of hydrocarbon fuels consists in the fact that contemporary fuels have come very close to their limit as regards this characteristic (see Table 3).

TABLE 26.

Heats of Formation of Theoretical Working Mixtures of Various Fuels [13]

| 1 Топливо | 2. Теоретически необходимое количество воздуха для сгорания 1 кг топлива, кг | 3 Теплота сгорания рабочей смеси при α = 1 и 760 мм рт. ст., ккал/м³ |
|---|---|---|
| 4 Бензин авиационный . . . | 15,0 | 824 |
| 5 Бензин автомобильный . . | 15,0 | 826 |
| 6 Керосин тракторный . . . | 15,0 | 832 |
| 7 Пиробензол . . . . . | 14,0 | 822 |
| 8 Этиловый спирт (ректификат) . . . . . | 9,0 | 821 |
| 9 Метанол . . . . . | 6,53 | 823 |

1) Fuel; 2) theoretically necessary quantity of air for combustion of 1 kg of fuel, kg; 3) heat of combustion of working mixture with $\alpha = 1$ and 760 mm Hg, cal/m$^3$; 4) aviation gasoline; 5) automobile gasoline; 6) tractor kerosene; 7) pyrobenzene; 8) ethyl alcohol (rectificate; 9) methanol.

However, the possibilities for increasing the heats of combustion of such fuels should not be regarded as having been completely exhausted if, in specifying them, we follow a more rational system based upon the creation of recipes for fuels of specific compositions from hydrocarbons of specified chemical composition.

Let us examine the role taken by the heat of combustion of the fuel in the operation of modern engines.

The heat of combustion of the mixture entering a reciprocating internal-combustion engine is approximately the same irrespective of the chemical composition of the liquid fuel and, consequently, irrespective of its heat of combustion (Table 26).

For this reason, the power output of a piston engine undergoes virtually no change as a result of using a fuel with a different heat of combustion.

When a fuel with a higher heat of combustion is used, more air will

be used for combustion of a unit weight of combustible; in other words, the working mixture will be leaner; when a fuel with a lower heat of combustion is employed, the mixture will be richer.

Consequently, the use of a fuel with an elevated heat of combustion in piston engines results in a drop in the specific fuel consumption, a decrease in fuel-tank capacity required for the same range of the vehicle, and a slight change in the jet section in accordance with the quantity of fuel supplied, but does not result in a change in engine power.

Irrespective of the heat of combustion of its fuel, the power developed by a piston engine reamins constant.

For jet and rocket engines, the thrust of which is created solely through the reaction forces of the gases issuing from the nozzle, the fuel's heat of combustion is a more important factor.

The thrust of an air-breathing jet engine is the resultant of the air- and gas-flow forces acting on the elements of the engine's flow-through section and outer surface. It is directly proportional to the quantity of air passing through the engine and to the outflow speed of the gases passing through the reaction engine's nozzle.

The consumption of fuel by weight is only 1.5 to 2% of the weight of air consumed. The basic function of the fuel is to increase the kinetic energy of the air, which is expended on useful work and compensation of losses. Consequently, the higher the fuel's heat of combustion, the larger will be the useful work done by the engine.

To attain high efficiency in an air- breathing jet engine, it is necessary to use a fuel with the highest possible heat of combustion; this will make it possible to increase the volume of the gases and, consequently, their outflow velocity.

The importance of increased heats of combustion for jet fuels [illegible]

become even clearer if we recall that the heat lost with the exhaust gases comes to 70 to 75% of the heat liberated in combustion of the fuel, while only 14 to 17% of the heat is used at the present time on useful work [14].

Consequently, the use of a fuel with an elevated heat of combustion in air-breathing jet engines results not only in the advantages listed for piston engines, but also in an increase in engine power and the range and speed of the aircraft, or a decrease in specific fuel consumption.

For a rocket engine, the importance of a fuel with a high heat of combustion is even greater. The altitude ability of a rocket engine increases by as many times as the fuel's heat of combustion is increased. The use of a fuel with a higher heat of combustion for rocket engines results not only in the advantages listed for air-breathing jet engines, but also in an increase in the rocket's altitude ability.

The total quantity of heat liberated on combustion of the fuel present in an engine's tanks or in any other reservoir may be expressed in either of two ways:

1) the product of the unit-weight heat of combustion by the weight of fuel;

2) by the product of the unit-volume heat of combustion by the volume of fuel.

For a given fuel, these quantities are equal and there is therefore no necessity of using the two values — the unit-weight and unit-volume heats of combustion — simultaneously.

In practice, only the unit-volume heat of combustion is convenient to use in cases where the fuel-tank capacity is limited and the fuel tanks are filled to the brim when operation of the engine begins. Here it is unnecessary to know the unit-weight heat of combustion of the fuel.

Only the unit-weight heat of combustion is conveniently used in cases where fuel-tank capacity is sufficiently large and may not be completely filled with fuel, as well as when the specific gravity of the fuel is so high that the possibility of overloading the aircraft with fuel must be considered. Here it is not necessary to know the value of the fuel's unit-volume heat of combustion.

Consequently, we may use either the unit-volume or the unit-weight heat of combustion of the fuel, depending on the mission involved.

It must be remembered that an aviation fuel with an elevated density will take preference only where the increase in heat of combustion outweighs the loss of the energy that must be expended as a result of the increased flight weight of the aircraft when the latter is loaded with the heavier fuel.

The criterion for energy evaluation of a fuel will be the specific heat of combustion of the fuel loaded referred to a unit of the machine's flight weight.

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[List of Transliterated Symbols]

198 н = n = nizshaya = lower

200 в = v = vysshaya = upper

## Chapter 8

## SCALING AND VARNISH-FORMING ABILITIES OF FUELS

### SCALE

Scale is a term applied to the solid carbonaceous materials that form during operation of internal-combustion engines on the walls of the combustion chamber, the piston heads, the upper land of the piston up to the first compression ring, on the valves and on the spark plugs. In reciprocating engines, scale is deposited on the components in the form of a relatively thin layer only a few millimeters thick and having a rough surface. In jet engines, the thickness of the scale formed on the combustion-chamber walls may reach several centimeters.

The color of the scale is usually black, but it may also assume any other color – red, brown and even white; it all depends on the materials that form it.

Scale may be formed from either the fuel or the oil. In the antechambers of diesels, to which oil has virtually no access, and in the combustion chambers of jet engines when the fuel is burned without any oil additive, scale of purely fuel origin is deposited on the walls. In compressors, the scale is formed solely from the oil. In carburetor engines, and in the main combustion chambers of diesels, scale is formed from fuel and oil simultaneously.

Depending on the engine's operating conditions, the temperature of the surface onto which the scale is deposited, the quality of the fuel and oil, and the materials entering the combustion chamber to-

gether with the air, fuel and oil, the composition and properties of the scale deposits vary. Consequently, different types of scale are deposited on different components even in the same combustion chamber; the scale formed on the intake valve differs from the scale formed on the exhaust valve, and the valve scale differs, in turn, from the scale formed on the piston head and on the combustion-chamber walls. Further, different layers of the same scale differ from one another as regards chemical composition.

Scale consists of carbon, oxygen, hydrogen and other elements (iron, lead, silicon etc.), the quantity of which may vary over a very wide range. For example, when an engine is operated on unethylated gasoline, the scale removed from the piston dome consists approximately of 72-72% carbon, 17-20% oxygen, and 4-5% of hydrogen; the noncombustible part of the scale, on the other hand, amounts to only a few percent. However, in the case of engine operation on leaded gasoline, the scale may be found to contain an much as 60-90% of lead compounds. It is customary to characterize scale on the basis of its chemical composition, expressing its components in terms of their percentages: oil, asphaltenes, carbenes, carboids and ash. If necessary, the ash is analyzed for qualitative and quantitative determination of its contents of various elements (iron, lead, barium, silicon and others).

There are two possible ways in which scale may form in internal-combustion engines: 1) as a result of deposition of carbon black on the components together with various compounds that form on combustion of fuel and oil vapors; 2) as a result of the profound changes to which the fuels and oils are subject when, in liquid form, they strike the hot parts of the engine. These two routes of scale formation in internal-combustion engines are intimately interrelated.

Not all of the scale that forms on combustion of the fuel re-

mains on the components. The basic mass is carried out of the combustion chamber together with the exhaust gases, some quantity of it enters the crankcase, and only a very minor fraction of all of the scale formed remains on the combustion-chamber components. We would therefore draw a distinction between the scaling ability of a fuel and the quantity of scale that is deposited on the components, since the latter depends not only on the fuel, but also on a number of other factors.

Influence of Fractional Composition on Scaling Ability of Fuel

It is a general qualitative rule for all fuels, irrespective of the type of engine for which they are intended, that their tendency to scaling rises as their fractional composition becomes heavier.

TABLE 27

Scaling Abilities of Various Fuels [1]

| 1 Топливо | 2 Температура выкипания 10%, °С | 3 Вес нагара, г |
|---|---|---|
| 4 Авиабензин | 62 | 0,19 |
| 5 Керосин | 173 | 0,83 |
| 6 Дизельное топливо I | 238 | 1,79 |
| 7 Дизельное топливо II | 249 | 1,79 |

1) Fuel; 2) temperature of 10% distillation, °C; 3) weight of scale, grams; 4) aviation gasoline; 5) kerosene; 6) diesel fuel I; 7) diesel fuel II.

Using a laboratory apparatus that reproduced the basic parameters of a gas-turbine engine's combustion chamber, Starkman, Cataneo and Allister investigated the scaling ability of commercial fuels of various fractional compositions [1]. The results that they obtained (Table 27) indicated that the tendency of commercial fuels to form scale increases as their vaporizability diminishes and their fractional compo-

sitions become heavier.

It was also established in tests run on this laboratory apparatus with various individual hydrocarbons that the tendency of paraffinic, naphthenic and aromatic hydrocarbons to form scale diminishes with diminishing boiling point.

Shore and Ockert [2] studied the mechanism of scaling and the influence of fuel fractional composition with the aid of radioactive isotopes. They showed that as the boiling point of the hydrocarbons rises, their tendency to scale also rises, with this increase becoming most distinctly expressed at a boiling point of about 200°. It was found that 98.3% of the entire quantity of gasoline introduces only 35% of the entire hydrocarbon part of the scale, while the remaining 65% of the scale is formed by the tailings of the gasoline, which amount to only 1.7%.

Investigation of a series of commercial fuels by the PZI method has shown that a Type T-1 fuel with a boiling range of 128 to 279° has a scaling ability of the order of 100 to 140 mg/kg, while the heavier diesel-type fuels (179 to 350°) give 245 to 265 mg/kg and solar oil, which boils in the range from 300 to 365°, gives 360 mg/kg [3].

The present authors obtained similar results with the assistance of A.A. Gureyev in investigating four thermal-cracking gasolines with various fractional compositions in an automobile engine equipped with scaler inserts [4]. All four gasolines were produced from the same initial specimen by separation of the high-boiling fractions by simple rectification. These gasolines showed only minor practical differences as regards their group chemical composition. As the fractional composition of the gasoline became lighter, however, its tendency to scale formation dropped off sharply (Table 28).

In earlier studies, investigators did not always find a link be-

tween the vaporizability of fuels and their tendency to form scale, particularly when they were comparing gaseous fuels such as natural gas and hydrogen with gasoline. For example, Buman [5] found no marked difference in scaling properties in tests of hydrogen and aviation gasoline in a single-cylinder apparatus. According to Gruse [6], the wide variations in the vaporizability of both fuels – ranging from that of natural gas to that of gasoline with a terminal boiling point of 225° – exerted no noticeable influence on scaling in an engine in operation with a constant excess-air ratio. The quantity of scale removed from the cylinder head and referred to 1 liter of oil consumed remained practically constant. But the author notes in this connection that a considerable increase in scaling was observed in operation on heavier fuels – ligroin and kerosene – as a result of poorer carburetion of the fuel and the lower flame temperature.

TABLE 28

Influence of Fractional Composition of Thermal-Cracking Gasoline on Its Scaling Ability

| 1 Бензины термического крекинга | 2 Плотность $\rho_4^{20}$ | 3 Фракционный состав, °С | | | | | 6 Йодное число, г йода/100 г бензина | 7 Углеводородный состав, % | | | 11 Нагарообразующая способность, мг/час |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 4 н. к. | 10% | 50% | 90% | 5 к. к. | | 8 непредельные | 9 ароматические | 10 нафтены и парафины | |
| 12 Исходный с к. к. 205° | 0,749 | 67 | 102 | 138 | 192 | 205 | 79,8 | 28 | 1,0 | 71,0 | 50 |
| 13 Тот же бензин с к. к. 190° | 0,745 | 65 | 94 | 130 | 175 | 190 | 79,0 | 35 | 0,5 | 64,5 | 33 |
| 14 Тот же бензин с к. к. 175° | 0,734 | 61 | 84 | 112 | 156 | 175 | 86,0 | 37 | 0,0 | 63,0 | 23 |
| 15 Тот же бензин с к. к. 160° | 0,726 | 56 | 65 | 103 | 146 | 160 | 89,0 | 37 | 0,0 | 63,0 | 20 |

1) Thermal-cracking gasoline; 2) density $\rho_4^{20}$; 3) fractional composition, °C; 4) start of boiling; 5) end of boiling; 6) iodine number, g of iodine/100 g of gasoline; 7) hydrocarbon composition, percent; 8) unsaturated; 9) aromatic; 10) naphthenes and paraffins; 11) scaling ability, mg/hour; 12) initial gasoline, final boiling 205°; 13) same gasoline, final boiling 190°; 14) same gasoline, final boiling 175°; 15) same gasoline, final boiling 160°.

The existence of contradictory data is apparently to be accounted for by the deficiencies of the methods used earlier, which did not permit ascertaining the differences between the scaling abilities of fuels with only slightly different vaporizabilities.

At the present time, most researchers come to the conclusion that (all other conditions the same) fuels of heavy fractional composition are more inclined to form scale than are fuels of light fractional composition.

Influence of Chemical Composition on Scaling Ability of Fuel

The scaling ability of a fuel depends heavily on its chemical composition. Researchers have noted a particularly distinct rise in tendency to scale in the aromatic hydrocarbons.

In an investigation of the influence of the structure and boiling point of a hydrocarbon on its tendency to form scale in internal-combustion engines, Shore and Ockert [2] added the hydrocarbons to be studied to the fuel after tagging them with radioactive carbon. The activity of the scale was measured after the tests and the extent to which the hydrocarbons investigated had participated in scaling was determined (see below on foreign techniques).

They found that with identical boiling points of the hydrocarbons, the paraffins manifest the least tendency to form scale, followed by the naphthenes and olefins. The aromatic hydrocarbons and the bicyclic hydrocarbons in particular showed the strongest tendency to scaling. The scaling abilities of the aromatic hydrocarbons is approximately 3 times that of paraffinic hydrocarbons with the same boiling point.

Investigations of scaling by mixtures of cetane (in mg/kg) with α-methylnaphthalene by the PZI method [3] showed that as the content of α-methylnaphthalene in the mixture increases, its scaling tendency

increases [2].

| | |
|---|---|
| Cetane (standard) | 110 |
| 80% cetane + 20% α-methylnaphthalene | 125 |
| 60% cetane + 40% α-methylnaphthalene | 215 |
| 40% cetane + 60% α-methylnaphthalene | 230 |

In a test of B-70 aviation gasoline mixed with benzene and toluene in an automobile engine, scaling increased with increasing content of aromatic hydrocarbons in the gasoline.

It was shown by the investigations of Spindt and Wolfe [7] on a two-cylinder Galf [sic; Half?] engine in which one piston had been replaced by an equalizing mechanism in conjunction with a special 40-hour procedure that paraffins and olefins exert insignificant influence on the tendency of the fuel to form scale. Complex diolefins and aromatic hydrocarbons with olefinic chains, on the other hand, aggravate the scaling properties of the fuel considerably. Selective purification ($SO_2$) enabled them to reduce the aromatic-hydrocarbon content in the fuel from 31 to 17%; the content of unsaturated hydrocarbons dropped unnoticeably when this was done. However, the scaling ability of the fuel showed virtually no change. On the basis of these experiments, they concluded that the unsaturated hydrocarbons determine the fuel's tendency to form scale to a considerably greater degree than do the aromatic hydrocarbons.

Strongly branched aliphatic hydrocarbons (diisobutylene and isopentenes) produce only an insignificant increase in scaling. Although it polymerizes easily, styrol does not produce an increase in the deposits; α-methylstyrol (an aromatic olefin) increases scaling considerably.

The basic source of scaling, according to the results of these researches, is the diolefin content. On addition of tert-butyl peroxide to the fuel, it was found that the hydroperoxides, which increased

the rates of oxidation reactions, contribute to a considerable increase in the fuel's scaling tendency (Fig. 56).

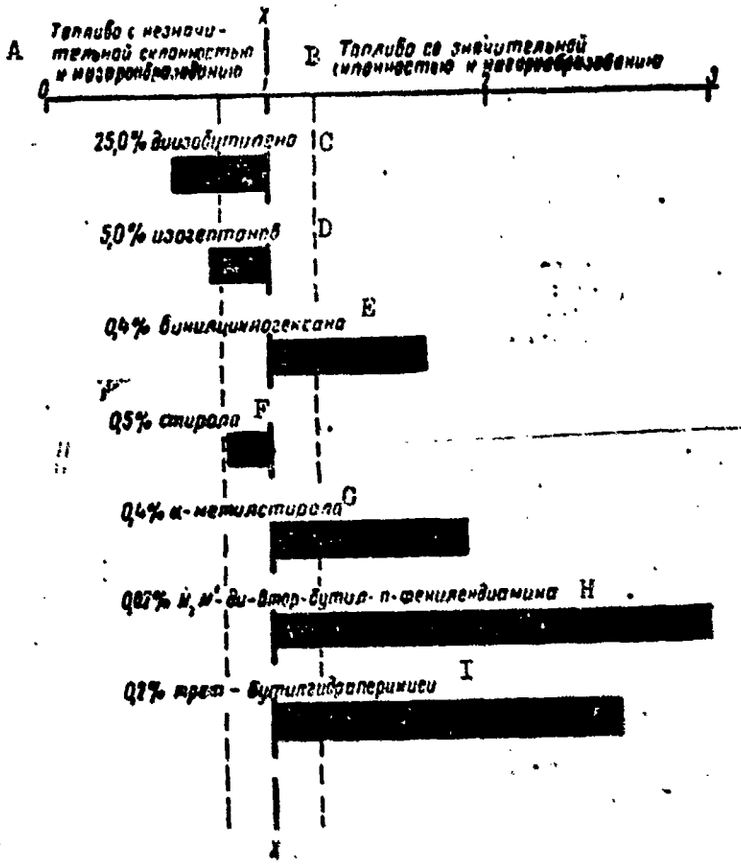


Fig. 56. Changes in scaling ability of fuel on addition of various hydrocarbon compounds. X – X is the line for the standard fuel, taking the error range into account. A) Fuel with minor tendency to scaling; B) fuel with considerable tendency to scaling; C) 25.0% diisobutylene; D) 5.0% isoheptanes; E) 0.4% vinylcyclohexane; F) 0.5% styrol; G) 0.4% α-methylstyrol; H) 0.02% N,N'-di-sec-butyl-p-phenylenediamine; I) 0.2% tert-butyldihydroperoxide.

In investigating various individual hydrocarbons and commercial fuels in the combustion chamber of an air-breathing jet engine, Ya.M. Paushkin showed [8] that with increasing ratio of carbon to hydrogen in the fuel, the scaling ability of the fuel increases. It was noted simultaneously that the tendency of the fuel to form scale increases

as its boiling point increases.

Influence of Ethyl Fluid on Scaling Ability of Fuel

Of all of the fuel additives used, the antiknock compound tetraethyl lead exerts the strongest influence on scaling [9].

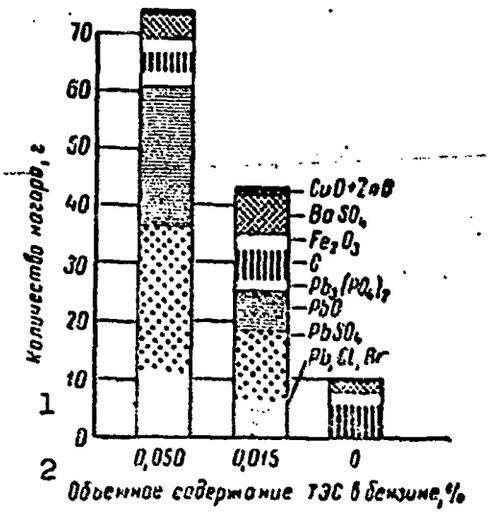


Fig. 57. Influence of tetraethyl lead on composition and quantity of scale in combustion chamber. 1) Quantity of scale, g; 2) volume content of tetraethyl lead in gasoline, %.

When ethylated gasolines are burned, amounts up to about 2% of the lead present in the original gasoline remain in the engine. Considerable quantities of various lead compounds accumulate in the scale (Fig. 57). As a result, several times the amount of scale deposited in operation on unethylated gasolines is deposited in the combustion chambers of engines burning ethylated gasolines.

As a rule, scaling in the engine increases with increasing concentration of tetraethyl lead in the fuel, and this applies with equal force for both the initial stages of scaling and for scale that has already reached its equilibrium state.

Influence of Sulfur on Scaling Ability of Fuel

In the opinion of most investigators, the tendency of a fuel to scale formation increases with increasing sulfur content in the fuel [10]. This was demonstrated in 220-hour stand tests of four-cylinder carbureted engines that were carried out at the NAMI (Table 29).

According to Gibson et al. [11], scaling also increases in an automobile engine with increasing content of sulfur in an ethylated gasoline consisting of a mixture of cracking and direct-distilled gasolines.

| | | |
|---|---|---|
| Quantity of sulfur in ethylated gasoline, % | 0.05 | 0.30 |
| Weight of scale formed in engine during 100-hour test, g: | | |
| in steady operation . . . . . | 75 | 112 |
| in variable operation . . . . . | 56 | 84 |

TABLE 29

Influence of Quantity of sulfur in gasoline on its scaling ability

| 1 Содержание серы в бензине, % | Количество нагара, г 2 | 3 Увеличение |
|---|---|---|
| 0,046 | 1,9 | 4 — |
| 0,100 | 2,93 | в 1,5 раза |
| 0,200 | 4,26 | » 2,5 » |
| 0,357 | 5,67 | » 3,0 » |

1) Content of sulfur in gasoline, %; 2) quantity of scale, g; 3) increase; 4) by a factor of 1.5.

In tests on sulfur-containing diesel fuels burned in a D-35 tractor engine, N.G. Puchkov [12] found a considerable increase in the quantity of scale on the piston dome (in grams) as the sulfur content in the fuel increased.

| | |
|---|---|
| Standard sulfur-free fuel . . . . | 5.4 |
| Fuel containing 0.58% sulfur . . . . | 12.4 |
| Fuel containing 0.89% sulfur . . . . | 18.1 |

TABLE 30

Influence of Hydraulic Purification of Fuel on Scaling

| 1 Топливо | 2 Количество нагара, г | |
|---|---|---|
| | 3 на днище поршня | 4 на верхнем пояске гильзы цилиндра |
| 5 Содержащее 1.0% серы (до гидроочистки) . . . | 0.86 | 1.5 |
| 6 Содержащее 0.03% серы (после гидроочистки) | 0.54 | 0.63 |

1) Fuel; 2) quantity of scale, g; 3) on dome of piston; 4) on upper band of cylinder sleeve; 5) containing 1.0% of sulfur (before hydraulic purification); 6) containing 0.03% of sulfur (after hydraulic purification).

Similar data were obtained by I.I. Gershman and I.A. Traktovenko [13] in 500-hour tests of a lightened diesel fuel containing 0.46% of sulfur and a standard fuel containing 0.05% of sulfur in a two-cycle YaAZ-204 automobile diesel. In operation on the high-sulfur fuel, approximately one and one-half times as much scale formed on the engine

components than formed with the standard fuel, despite the fact that the latter had a somewhat heavier fractional composition.

As a result of 100-hour tests on fuels from sulfur-bearing petroleums in marine diesels, M.S. Smirnov [14] showed that when the sulfur content in the fuel is reduced by hydraulic purification from 1% to 0.03%, scaling is reduced by a factor of 1.5 to 2 (Table 30).

Sulfur present in the fuel influences not only the quantity of scale formed, but its properties as well. Sulfur compounds accumulate in the scale and raise its density [15].

| | | |
|---|---|---|
| Quantity of sulfur in fuel, % . . . . . | 0.08 | 1.50 |
| Quantity of sulfur in scale, % . . . . . | 1 | 9 |
| Density of scale, g/cm$^3$ . . . . . | 0.03 | 0.50 |

CONSEQUENCES OF SCALE FORMATION

Scale on combustion-chamber walls has a detrimental influence on the processes unfolding in the engine and, among other things, results in reduced efficiency, power and economy of the engine, raises the requirements as to the antiknock properties of the fuel, disturbs the normal combustion process as a result of uncontrolled premature and surface ignition, in which the impact loads on the engine components increase and its operating reliability drops sharply, and causes misfiring in the ignition system and burning of the valves.

Power Losses

As a result of scale formation in the combustion chamber, the size of the combustible mixture drawn in is reduced and the indicated and effective efficiencies decline, with the result that the engine loses power.

The influence of scaling in reducing the power of the engine depends considerably on the engine's operating conditions. According to Paige and Mueller [16], more scale forms under steady operating conditions with a given fuel and a given oil than in a variable operating

regime; the magnitude of the power lost in the steady mode is accordingly also larger.

The use of various grades of fuels and oils over a wide range produces even more rapid scaling and, accordingly, causes larger power losses (Fig. 58). In a number of cases, the power loss due to scaling reaches 10 – 14% when ethylated gasolines are used.

Increase in Required Gasoline Octane Number

Operating practice with internal-combustion engines has established that as mileage is accumulated with a motor vehicle or when an engine operates for a long time under the same conditions, the required octane number of the gasoline rises as a result of scale formation.

The increased tendency of the engine to knock due to scale formation is accounted for firstly by the poor thermal conductivity of the scale, which leads to a rise in the temperature of the gaseous mixture and the surface of the scale on the combustion-chamber components and accelerates the oxidation reactions that contribute to detonation; secondly, by the decreased combustion-chamber volume and the corresponding increase in the engine's compression ratio; thirdly, by the catalytic effect of the scale, which gives rise to chemical reactions that produce detonation.

Depending on the operating conditions of the engine and the scaling ability of the fuel, the required octane number rises by an average of 7 to 17 units [17] and, in some cases, by 28 octane units [18].

Tetraethyl lead in the gasoline causes different changes in the required octane number in accordance with the operating conditions of the engine. Operational tests of six motor vehicles [19] on unethylated gasoline and on gasoline containing 0.4 and 1.1 ml of tetraethyl lead per 1 kg (two automobiles operated on each fuel) established that

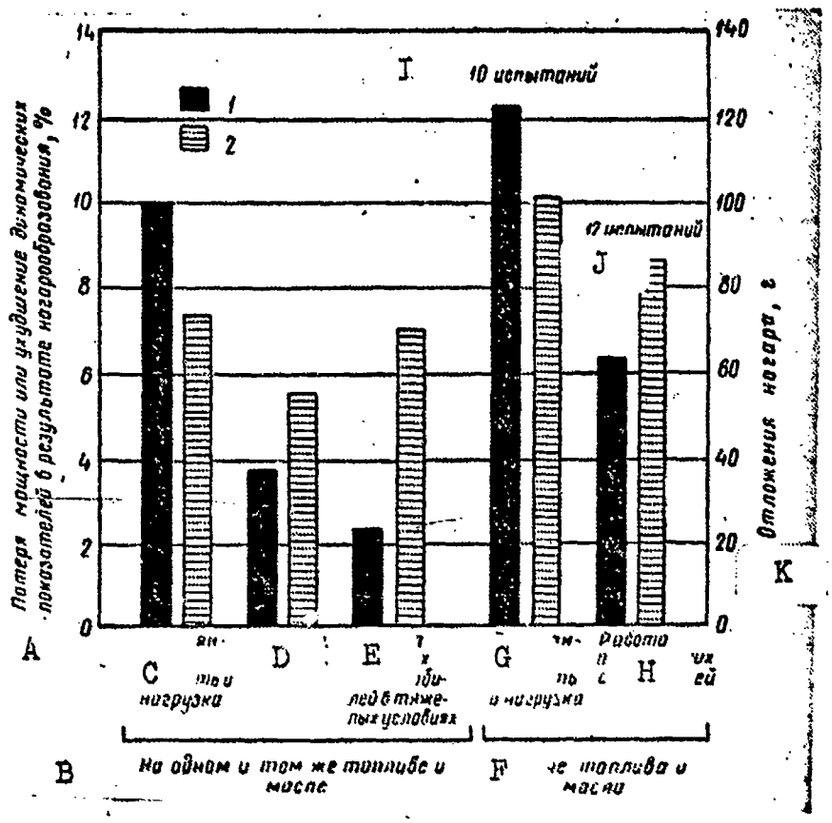


Fig. 58. Power loss as a result of scaling under various sets of engine operating conditions. 1) Power loss; 2) scale weight. A) Power loss or deterioration of dynamic indices as a result of scaling, %; B) operation on one fuel and one oil; C) constant speed and load; D) variable; E) operation of trucks under severe conditions; F) various fuels and oils; G) constant speed and load; H) operation of passenger automobiles; I) 10 tests; J) 12 tests; K) scale deposit, g.

in operation on ethylated gasoline, the requirements for antiknock properties in the fuel rose most rapidly during the first 6400 km and reached a maximum at about 8000 km; the figure then remained unchanged in further tests. In operation on unethylated gasoline, the maximum had not been reached even at 16,000 km.

Incandescence Ignition

Detonation due to premature ignition of the mixture by glowing scale particles may be observed in high-compression engines. This effect is superficially similar to ordinary detonation, but is accompanied by a more ringing knock and is unstable from cycle to cycle. It may be eliminated by using a gasoline with a weaker tendency to scaling, special additives that modify the scale, or higher-octane gasolines [20]. Another disturbance to the combustion process in the engine as a result of incandescence ignition – namely, simultaneous ignition of the mixture at several points of the combustion chamber by incandescent scale particles – has come to be known as surface ignition.

Strictly speaking, surface ignition implies an abnormal combustion process of the mixture in the combustion chamber that is accounted for by the appearance of a flame front not as a result of normal ignition from the plug spark, but as a result of ignition at any hot spot or surface. Glowing scale particles and overheated combustion-chamber elements (valves, spark-plug housings, etc.) may form such ignition sources. Surface ignition occurs in two forms: 1) ignition that occurs before the spark, which is known as premature ignition, and 2) ignition arising after the ignition spark has appeared (in advance of the flame front), which is known as delayed ignition.

Surface ignition of the mixture results in a very rapid and "hard" course of the combustion process and is accompanied by loud knocks at a frequency lower than that of detonation (500 to 1600 and 5000 to 10,000 cycles, respectively); in this case, combustion is characterized by a higher rate of pressure increase, a higher maximum pressure, and displacement of the maximum pressure toward top dead center.

Surface ignition imposes impact loads on the components, reduces the efficiency of the engine by 13% [21, 22], results in overheating and damage to the components, sharply reduces the gain achieved by using higher compression ratios, and lowers the operating dependability of the engine as a whole.

The use of tetraethyl lead to increase the antiknock property of gasolines contributes simultaneously to the appearance of surface ignition in the engine. The intensity of surface ignition reaches such significant levels in many cases that it completely nullifies the antiknock effect of the tetraethyl lead. The increased tendency of ethylated gasolines to incandescence ignition is accounted for by the fact that certain lead compounds catalytically lower the ignition temperatures of the carboniferous scale deposits. For example, the self-ignition temperature of carbon (carbon black) in the presence of lead compounds is reduced from 500 to 200 - 230°; scale particles in the combustion chamber begin to glow and assume temperatures high enough to cause premature ignition of the mixture.

In addition to increasing scaling, the presence of aromatic hydrocarbons in the fuel also causes a marked rise in its tendency to incandescence ignition in the engine [23, 24]. Jonson ran tests on a motor vehicle into which an engine with a 10-to-1 compression ratio had been installed, under conditions simulating city driving. The tests were conducted on an aromatic fuel with a research octane number of 106. After the automobile had traveled certain distances, the intensity of incandescence ignition was evaluated by the number of incandescent flashes (Fig. 59). Here it was established that as mileage and scale accumulated, the intensity of incandescence ignition increases; here, the number of incandescent flashes was approximately 1.5 to 2 times as large with aromatic fuel than with paraffinic fuel,

although the octane number of the aromatic fuel was 1 point higher than that of the paraffinic. According to Hopkins, Pecora and Alpert [24], the intensity of incandescence ignition was approximately 50 per cent higher when a fuel containing 30% of aromatic hydrocarbons was

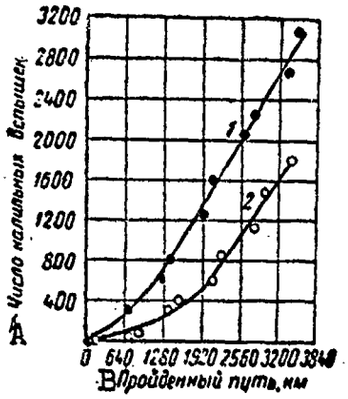


Fig. 59. Variation of number of incandescent flashes as a function of distance traveled. 1) Aromatic fuel, research octane no. 106; 2) paraffinic fuel, research octane no. 105. A) Number of incandescent flashes; B) distance traveled, km.

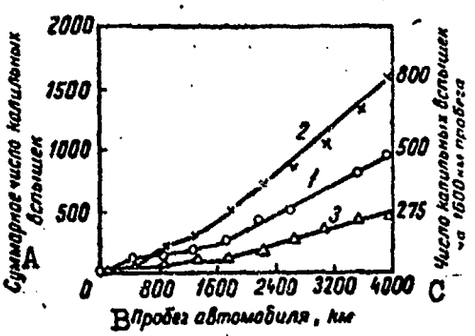


Fig. 60. Results of tests on engine with spherical combustion chamber and compression ratio of 12 running on various fuels. 1) 0% of aromatic hydrocarbons; 2) 30% of aromatics; 3) 30% of aromatics with additive (0.4%). A) Total number of incandescent flashes; B) mileage on vehicle, km; C) number of incandescent flashes at 1600 km.

used.

The same authors also indicated that the addition of a phosphate additive in an amount of 0.4% to the aromatic fuel reduced the intensity of incandescence ignition in the engine considerably (Fig. 60).

In the presence of the phosphorus compounds, lead-phosphorus complexes form; unlike the lead compounds, these caused only an insignificant drop in the ignition temperature of the carbon and thereby reduced the ability of the scale to act as a source of mixture ignition in the cylinder.

A boron additive also reduces surface ignition by softening the scale deposited on the hot surfaces of the engine's combustion chamber; once the scale is softened, it is scavenged out more easily and the self-cleaning action of the engine is improved. A particularly sharp reduction is observed in the deposition of lead scale on the exhaust valves when a boron additive is used with ethylated gasolines.

Spark-Plug Misfiring

Deposition of lead compounds on the electrodes of the spark plugs results in short circuiting, so that the engine begins to miss and its power drops noticeably.

Scaling on the spark plugs of aviation engines has resulted in airplane crashes [25].

The importance of this problem in automotive transportation is indicated by the results of tests on 150 vehicles, over 40% of which had trouble due to spark plug failure resulting from scaling and scratching of the contacts [20].

METHODS OF EVALUATING SCALING ABILITY OF FUELS

Soviet Methods

Two standard laboratory methods for indirect evaluation of fuel scaling ability are known: the method in which the cokability of the 10% fuel residue is determined (GOST 5061-49) and the method involving determination of the smokeless-flame height (GOST 4338-48). The first method is used to get an arbitrary evaluation of the scaling properties of diesel fuels and the second for jet fuels (see Chapter 3). The indices obtained by these methods give a conception extremely remote from the actual scaling ability of the fuel. More dependable results are obtained when fuels are tested in single-cylinder or full-scale engines (although this is a more complex task).

Up to the present time, scaling has been determined in the major-

ity of cases by running long-term motor tests with subsequent dismantling of the engines to determine the quantity of scale that has

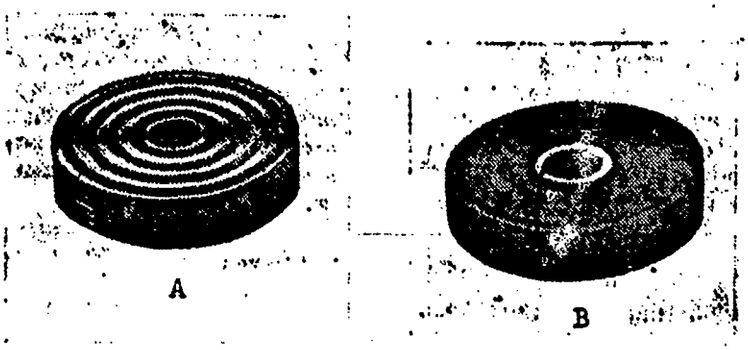


Fig. 61. General appearance of scaler. a) Clean; b) with scale.

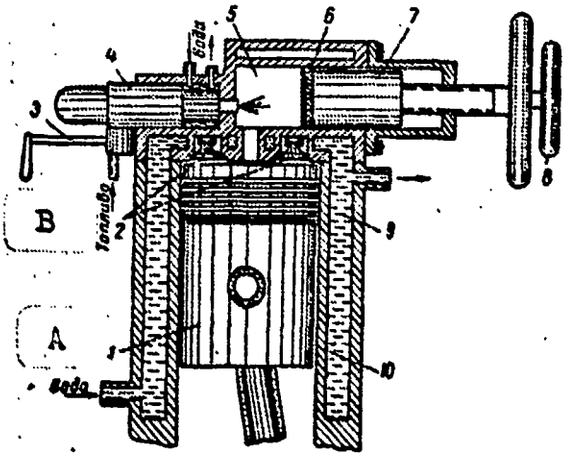


Fig. 62. Cylinder and antechamber of IT9-3 apparatus with scaler. 1) Piston; 2) valve; 3) nozzle pass valve; 4) nozzle; 5) antechamber; 6) scaler; 7) piston for varying compression ratio; 8) handwheel; 9) water jacket; 10) cylinder. A) Water; B) fuel.

formed on the components. In conducting prolonged tests, it is difficult to insure rigorously identical assembly and geometrical dimensions in the components of the various engines or even in the same engine before each test; it is difficult to maintain uniformity in the test conditions over many hours' engine operation, so that large discrepancies between the results are frequently observed even for parallel tests.

It should be noted in addition that running long-term tests is a complex and expensive operation. As a result, it becomes difficult and sometimes even impossible to establish an exact relationship for the scaling ability of a fuel as a function of various factors and, needless to say, the idea of running long-term tests on an engine every day for monitoring purposes cannot even be considered.

In the light of the above, a new method for evaluating fuel scaling ability that consists in the use of special interchangeable scalers secured to engine components merits special attention [3]. Use of the scalers enables us to restrict ourselves to short-term tests. Below we give a brief description of methods of evaluating fuel scaling properties on single-cylinder apparatus and on full-scale engines, using scalers.

PZI method for evaluating scaling abilities of kerosenes and diesel fuels

Essentially, the PZI method, which was developed by K.K. Papok, A.P. Zarubin and I.D. Inozemtsev, consists in running a 5-minute test on the fuel in a standard single-cylinder IT9-3 apparatus as used for determining cetane numbers. A special readily removable scaler – an aluminum disk with four concentric grooves on one of its faces (Fig. 61) – is bolted to the head of a small piston used in the engine antechamber to vary the compression ratio. The scaler's dimensions are as follows: diameter 41 mm, height 8 mm, width of groove (depression) 1.75 mm and depth of groove 2.5 mm. The scaler weighs 20 g, and the area of its involuted surface is 28 $cm^2$. A diagram of the cylinder and antechamber of the IT9-3 apparatus with the scaler secured to the piston head is shown in Fig. 62. After a 5-minute test in a rigorously maintained operating mode, the scaler is removed and the quantity of scale that has formed on it during the test is determined by weighing. The scaler is weighed before and after a test on an analytical balance accurate to the 4th decimal place.

The tests are carried out under the following conditions.

| | |
|---|---|
| Number of engine rpm | 900 ± 10 |
| Temperature of coolant, °C | 100 ± 2 |
| Compression ratio | 14.0 (constant) |
| Temperature of water cooling nozzle, °C | 38 ± 3 |
| Air temperature at intake, °C | 65 ± 1 |

| | |
|---|---|
| Fuel-injection pressure, kgf/cm$^2$ | 106 + 4 |
| Fuel-injection advance angle, degrees | 15 (before TDC) |
| Quantity of fuel injected, ml/min | 13 + 0.5 |
| Oil temperature in crankcase, °C | 50 = 65 |
| Oil temperature in line, kgf/cm$^2$ | 1.7 – 2.1 |

The other parameters of the engine (TDC, clearances, etc.) are maintained in conformity with GOST 3122-52 and the factory manual on operation of the IT9-3 apparatus. The average amount of scale on the scalers in accordance with the results of four 5-minute tests on each fuel is taken as an index to the scaling ability of the fuel and expressed in mg/5 minutes. The precision with which scale is determined between parallel tests is as follows: ±2 mg below 20 mg and ±10% above 20 mg. The investigations conducted by A.P. Zarubin and A.G. Slavinsky attest to the fact that fuels have different scaling abilities lying, for the specimens tested, in the range from 13 to 280 mg/5 min. Direct-distilled kerosenes have the lowest scaling abilities (13 – 18 mg/5 min), while certain types of solar oils (67 to 79 mg/5 min) and heavy catalytic-cracking gas oil (280 mg/5 min) have the strongest abilities.

| | |
|---|---|
| Pentane | 15 |
| Kerosenes: | |
| fuel T-2 | 13 |
| " T-4 | 13 |
| " T-1 | 16 |
| " TS-1 | 18 |
| " TR | 20 |
| cracking kerosene | 37 |
| Diesel fuels: | |
| DZ | 27 |
| DL | 30 |
| L | 35 |
| Surakhany gas oil (standard) | 33 |
| of thermal-cracking origin | 34 |
| with 1% sulfur (initial boiling 205°; 90% at 327°) | 37 |
| with 1.1% sulfur (initial boiling 180°) | 37 |
| with 1.25% sulfur (initial boiling 227°; 90% at 324°) | 55 |
| with 1.3% sulfur | 47 |
| Solar oils: | |
| Surakhany select petroleum | 39 |
| Balakhany and Binagadinsk [sic] petroleums | 67 |
| Balakhany petroleum | 79 |
| Catalytic gas oils: | |

light . . . . . 42
heavy . . . . . 280

TABLE 31

Scaling Ability of Various Mixtures of Diesel Fuels and Kerosenes*

| 1 Состав смеси | 2 Нагарообразующая способность, мг/5 мин | |
|---|---|---|
| | 3 расчетные данные | 4 экспериментальные данные |
| 5 Топливо ТС-1 + крекинг-керосин: | | |
| 60% + 40% | 26 | 25 |
| 30% + 70% | 32 | 35 |
| 6 плливо ТС-1 + соляровое масло из балаханской нефти: | | |
| 80% + 20% | 30 | 36 |
| 60% + 40% | 43 | 51 |
| 40% + 60% | 54 | 62 |
| 20% + 80% | 67 | 70 |
| 7 Дизельное топливо ДЗ + соляровое масло из бинагадинской и балаханской нефтей: | | |
| 70% + 30% | 47 | 46 |
| 30 + 70% | 55 | 67 |
| 8 Цетан + тяжелый газойль каталитического крекинга: | | |
| 85% + 15% | 55 | 51 |
| 70 + 30% | 95 | 107 |
| 9 50% дизельного топлива ДЗ + 50% легкого газойля каталитического крекинга | 35 | 32 |
| 10 50% газойля сураханского + 50% тяжелого газойля каталитического крекинга | 156 | 187 |

*The scaling abilities of the fuels taken for mixing were listed earlier.

1) Composition of mixture; 2) scaling ability, mg/5 min; 3) calculated data; 4) experimental data; 5) TS-1 fuel + cracking kerosene; 6) TS-1 fuel + solar oil from Balakhany petroleum; 7) diesel fuel DZ + solar oil from Binagadinsk and Balakhany petroleums; 8) cetane + heavy gas oil from catalytic cracking; 9) 50% DZ diesel fuel + 50% light gas oil from catalytic cracking; 10) 50% Surakhany gas oil + 50% heavy catalytic-cracking gas oil.

It is indicated on examination of the results from the scaling-ability determinations for the various groups of fuels that there are large differences between fuels of one and the same group. For example, kerosenes have a scaling ability ranging from 13 to 37 mg/5 min, while those of diesel fuels range from 27 to 55 mg/5 min and those of

solar oils from 39 to 79 mg/5 min.

To verify certain qualitative relationships of practical significance, investigations were conducted to ascertain the influence of fuel composition and certain fuel additives on scaling ability.

The results listed in Table 31 indicate that scaling ability varies additively in mixtures, i.e., the quantity of scale (in mg/5 min) obtained in determinations by the PZI method corresponds to the amounts figured arithmetically. This statement is of great practical importance in the production and compounding of diesel fuels. Knowing the scaling abilities of the components or fuels to be mixed, we may figure the scaling ability for the final product with sufficient accuracy. Moreover, this proposition may be employed in solving questions pertaining to selection of the most desirable diesel-fuel components.

It should be noted that this qualitative law applies only for fuels that do not contain additives.

The addition of the antioxidant additive tributyl phosphite (TBF) to diesel fuel resulted in a sharp increase in the scaling ability of this fuel. For example, a fuel with 1.4% of sulfur had a scaling ability of 42 mg/5 min; on addition of 0.5% of the TBF additive, this rose to 47 mg/5 min, and to 162 mg/5 min when 5% of TBF was added.

The PZI method is sensitive to fuel additives; this provides a basis for recommending it for research toward the creation of additives that lower the scaling abilities of diesel fuels and kerosenes.

Evaluation of scaling ability of diesel fuels using the 1Ch-10.5/13 marine engine

On the basis of the PZI method cited above, M.S. Smirnov and O.P. Yevdokimov developed a method for evaluating the scaling properties of diesel fuels using the 1Ch-10.5/13 single-cylinder marine engine [26].

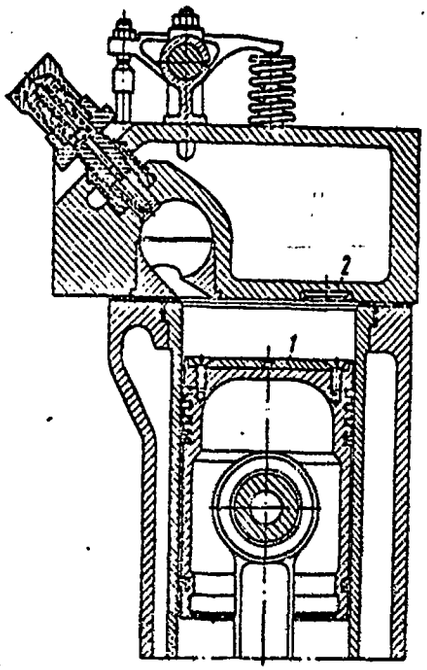


Fig. 63. Sectional drawing of scaler installation on piston head (1) and cylinder head (2) of 1Ch-10.5/13 engine.

Essentially, the method consists in installing a removable aluminum plate (scaler) with an effective area of 64 $cm^2$ on the piston head of the 1Ch-10.5/13 engine, and a second aluminum scaler with a working-surface area of 3.8 $cm^2$ on the cylinder head (Fig. 63).

The scaling abilities of diesel fuels as determined by this method are for the engine's rated speed (1500 rpm) and 75% load. The oil temperature in the crankcase is held in the range $65 \pm 5^{\circ}$; The cooling-water temperature is $55 \pm 5^{\circ}$ at the inlet and $80 \pm 2^{\circ}$ at the outlet. Every 15 minutes of operation of the engine, the scalers are removed and the quantity of scale formed on them determined by weighing. The engine operates for a total of 2 hours.

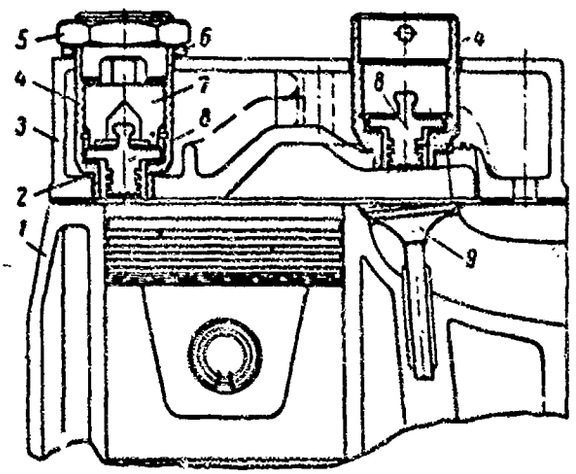


Fig. 64. Diagram of scaler installation in Type ZIL-120 engine. 1) cylinder block; 2) gasket; 3) cylinder head; 4) scaler receptacle; 5) nut; 6) gasket; 7) tensioning nut; 8) scaler; 9) exhaust valve.

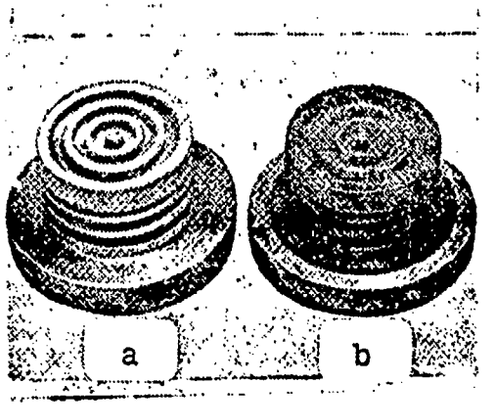


Fig. 65. Scalers. a) Clean; b) with scale.

The results of the test are expressed in the form of a curve indicating the change in the quantity of scale on the scalers in $mg/cm^2 \cdot 10^2$ as a function of the engine's operating time in minutes.

"PL" quick method for evaluating scaling ability of gasolines on full-scale engine

The essence of the method developed by K.K. Papok and S.M. Livshits consists in running a 1-hour fuel test on a full-scale engine fitted with removable scalers. Special receptacles (Fig. 64) are installed in the cylinder head of an automotive engine; these make it possible to install the removable aluminum scalers in the combustion chamber in 5 minutes without removing the cylinder head. The scaler weighs 24 g; it has an involuted surface area of about 24 $cm^2$. The general appearance of the scaler is shown in Fig. 65.

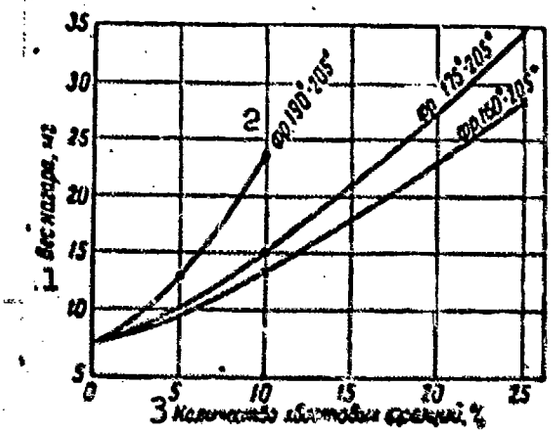


Fig. 66. Influence of tailings fractions from thermal cracking on scaling ability of direct-distillation A-56 automobile gasoline. 1) Weight of scale, mg; 2) 190 – 205°F; 3) quantity of tailings fractions, %.

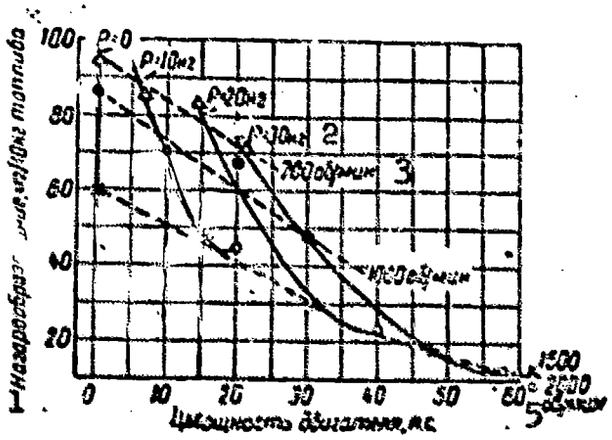


Fig. 67. Influence of engine speed, load and effective power on scaling. 1) Scaling, mg/10 kg of fuel; 2) P = = 30 kg; 3) 700 rpm; 4) engine power, hp; 5) rpm.

After the 1-hour test of the fuel, the scalers are removed and

the scaling ability of the fuel expressed in mg is determined from the change in their weight.

Together with A.A. Gureyev, we evaluated the scaling abilities of various fuels in a Type ZIL-120 engine equipped with a K-84 carburetor, using a 1-hour technique under the following conditions.

1. 55 min with a load P = 20 kg, n = 1600 rpm, $N_e$ = 32 hp, $G_m$ = = 9 ± 0.3 kg/hr, $\theta^\circ$ = 20 to 22° before TDC.

2. 5 min at idle with n = 1000 rpm.

The results of the tests indicated that direct-distillation gasolines possess the least tendency to scale, while thermal-cracking gasolines possess the strongest tendency.

| | |
|---|---|
| A-56 automobile gasoline | 25 |
| A-70 " " | 26 |
| A-72 " " | 13 |
| B-70 aviation gasoline | 9 |
| B-70 + 40% of benzene | 15 |
| B-70 + 40% toluene | 17 |
| A-56 + 0.1% of ionene | 24 |
| A-56 + 2.0 ml/kg of R-9 | 67 |
| Thermal-cracking gasoline | 48 |
| Catalytic-cracking gasoline | 17 |
| Direct-distillation gasoline | 7 |
| Thermal-cracking gasoline with initial boiling at: | |
| 205° | 50 |
| 190° | 33 |
| 175° | 23 |
| 160° | 20 |

With increasing content of thermal-cracking gasoline in direct-distillation gasoline, the scaling ability of the mixture (in mg/hr) rises.

| | |
|---|---|
| Direct-distilled gasoline | 7 – 8 |
| Direct-distilled gasoline + thermal-cracking gasoline: | |
| 80% + 20% | 14 – 16 |
| 60% + 40% | 22 – 25 |
| 40% + 60% | 30 – 34 |
| 20% + 80% | 39 – 44 |
| Thermal-cracking gasoline | 48 – 54 |

When tailing fractions from thermal cracking are added to direct-

distilled gasoline, the tendency of the fuel to form scale also rises (Fig. 66).

Data from the quick "PL" method can be used not only to evaluate the scaling ability of fuels, but also to study the influence of various factors on scaling in a specific engine.

The series of short-term tests run on a Type ZIL-120 engine operating on A-56 gasoline and industrial oil 50 made it possible to ascertain the influence of various parameters of the engine's operating mode on combustion-chamber scaling. It was established that as the effective power of the engine increased at a constant speed or under constant load, the tendency to scale diminished; here, scaling fell off more sharply at constant load with increasing effective power than at constant crankshaft speed (Fig. 67).

It will be seen from the figure that as speed increases from 700 to 1600 rpm with a constant load or effective engine power, the tendency to scale diminishes. However, a further increase in engine speed from 1600 to 2000 has no effect on scale formation.

The influence of the engine's temperature conditions, spark-advance angle, the composition of the mixture, and other operational factors on scaling was studied using this test technique; the influence of motor-oil quality and oil consumption on this index was also investigated.

The quick "PL" method may be used in research toward perfecting production and compounding techniques for new grades of automobile gasoline for projected engines, for selection of the most efficient tetraethyl-lead scavengers and for finding additives that assist in reducing combustion-chamber scaling.

Foreign Methods

Methods for indirect determination of scaling in engines are ex-

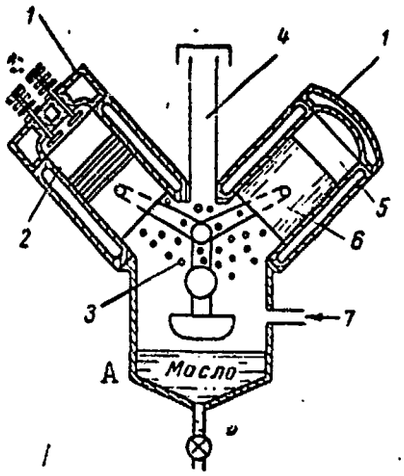


Fig. 68. Diagram of Galf two-cylinder laboratory engine. 1) Insulated water jacket; 2) power cylinder; 3) connecting-rod bearing; 4) crankcase ventilation (exhaust); 5) equalizing cylinder (nonoperating); 6) equalizing piston without head and piston rings; 7) crankcase ventilation (inlet). A) Oil.

tensively used in foreign practice. For example, a technique for evaluating the scaling abilities of fuels and oils based on determining the required octane-number increase or the variation of the frequency of incandescence flashes per unit time as functions of engine operating time is used widely.

Together with methods for indirect investigation of scaling in the engine with long-term tests under controlled and operational conditions, various methods are encountered in foreign practice for direct evaluation of fuel scaling properties in both long- and short-term tests.

Spindt and Wolfe [7] ran tests on a two-cylinder overhead-valve Galf laboratory engine, using a 40-hour test procedure under the following conditions.

| | |
|---|---|
| Speed, rpm | 2500 |
| Load, hp | 5.8 (nearly full load) |
| Ratio of air consumption to fuel consumption | 14 |
| Spark advance in degrees before TDC | 30 |
| Coolant temperature, °C | 32.2 |
| Oil temperature, °C | 65.6 |
| Oil load, g | 500 |
| Duration of experiment, hours | 40 |

The engine was equipped with a dual fuel system that made it possible to test two grades of fuel simultaneously (one grade in each cylinder) with the entire engine operating on one grade of oil.

The engine's cooling system permitted maintaining a specified coolant temperature in each cylinder, independently of the fuel temperature in the other cylinder.

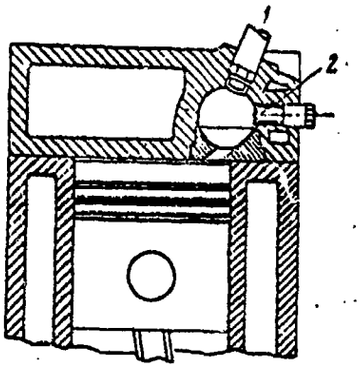


Fig. 69. Cylinder head of modified CFR test engine. 1) Fuel nozzle; 2) scaler disk.

In conducting the special tests, one of the Chevrolet pistons of the Galf laboratory engine was replaced by an equalizing piston that did not have a head or piston-ring grooves, as shown in Fig. 68. This laboratory apparatus was used not only to investigate the scaling properties of fuels and oils, but also to evaluate the role taken by the fuel and oil in scaling and for research into the influence of coolant temperature and other operational factors on scaling.

The tendencies of various diesel fuels to form scale was investigated by Hobson [27] using a standard CFR antechamber diesel with a constant compression ratio of 17:1.

The fuel nozzle was taken out of its normal axial position in the top of the antechamber and replaced with a plug having an interchangeable disk – a sampler similar to the scaler in the PZI method. The sampler was mounted flush with the inside surface of the antechamber [Fig. 69].

The temperatures of the oil (91 – 96°) and the coolant (99°) were held constant by means of immersion-type electric heaters. The engine was loaded with a synchronous generator having a power of 900 rpm [sic].

The engine was warmed up on standard fuel and then the fuel system was rinsed out with the test fuel; this was followed by installation of a weighed sampling disk that had been cleaned with a wire brush to a bright surface, and the engine was restarted. After the specified quantity of fuel (~300 g) had been burned, the engine was stopped and the disk removed for weighing and examination of the deposits that

had formed on it.

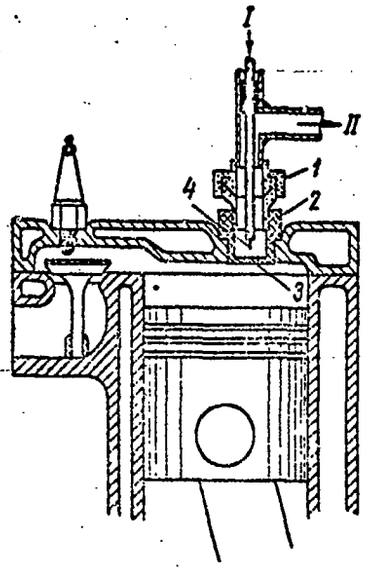


Fig. 70. Diagram of installation of radioactive sensor in combustion chamber of L-head engine. 1) Side arm; 2) radioactive sensor; 3) radioactive surface; 4) thermocouple. Lines: I) Coolant inlet; II) coolant outlet.

Tests were run with each fuel at various feed rates ranging from the maximum to the minimum at which faltering began. According to the author, the results of the tests were usually reproducible to within $\pm 5\%$.

During recent years, new methods of testing for the scaling properties of fuels and oils with the aid of radioactive indicators have been appearing with increasing frequency. Mingle and coauthors [28] proposed a radioactive method for investigating engine scaling that reduces to the following. A special sensor on which the surface facing the inside of the combustion chamber is covered with the radioactive isotope sulfur-35 or cobalt-60 is placed in the combustion chamber of a standard CFR engine with a compression ratio of 6.8 and an L-type cylinder head (Fig. 70).

The quantity of hydrocarbon deposits is judged from the lessening of emission from the radioactive surface of the sensor, as measured with special instruments.

The sensor is first calibrated by reference to standard absorbers with known absorbing capacity.

Unlike ordinary methods for evaluating scale formation, this method does not require disassembly of the engine and makes it possible to study the dynamics of the scaling process in the space of a few hours instead of several, tens or even hundreds of hours, as is required when ordinary long-term test methods are used.

The method makes it possible to study the influence of fuel quality, additives, and engine operating conditions on scaling.

When cobalt and certain other radioactive isotopes are used, it is necessary to observe industrial-safety rules and take special measures to protect the experimenters during the tests. From this standpoint, research methods in which low-energy radioactive isotopes are employed are of great practical interest.

Shore and Ockert [2] studied scaling in internal-combustion engines by adding to the gasoline a small quantity of the hydrocarbons that they wished to test after tagging the latter with radioactive carbon. The authors characterized the tendency of the test hydrocarbon to scaling in terms of the ratio of the content of the hydrocarbon in the scale to its content in the initial fuel prior to combustion. They determined this ratio indirectly by the so-called "degree of enrichment," which is the ratio of the specific radioactivity of the test hydrocarbon in the scale to its initial specific radioactivity in the initial fuel prior to the test. The higher the degree of enrichment of the fuel-component investigated, the greater is its tendency to form scale.

This method also enables us to ascertain the influence exerted on scaling by various carbon atoms in the molecule. According to the authors, the results are adequately reproducible. Sechrist and Hammen [29] also used a low-energy $\beta$-radiator in their investigations; this was carbon-14 with an extremely low activity level.

The specific radioactivities of the fuels that they tested did not exceed $10^{-8}$ millicurie/mg of carbon. They ran their tests on a single-cylinder CFR overhead-valve engine with a special model VN-14 Marvel-Schabler carburetor with a magnetic throttle control that made possible positive adjustment of the engine's operating periodi-

city in the variable mode. The tests were conducted during 48 hours at 900 rpm by separate cycles: 150 sec at full throttle and 100 sec at idle.

The change in required octane number was determined in the course of the tests. The engine was partially torn down after the tests. The combustion-chamber components were rinsed with a small quantity of isooctane to eliminate oil and loose scale. The wash liquid was then filtered and the residue weighed. The scale that had remained on the components was also cleaned off after washing and its radioactivity was evaluated.

Despite the difficulty of determining specific activity at such an extremely low level of specimen radioactivity, the authors nevertheless succeeded in determining with an admissible range of error the extent to which fuels and oils of various compositions and origins had participated in formation of scale on the piston dome and cylinder head.

The use of radioactive isotopes enables us to penetrate more deeply into the scaling mechanism and the influence exerted by specific fuel and oil components and hydrocarbon-molecule structure on scale formation.

VARNISH-FORMING ABILITY OF FUELS

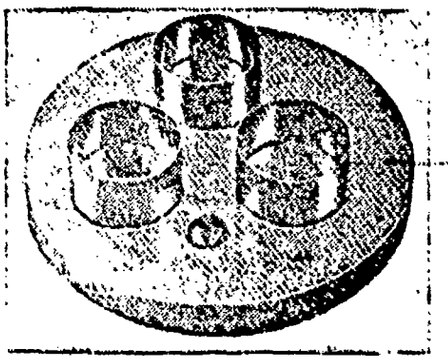

Fig. 71. Disk with cups.

In operation of an internal-combustion engine, varnish deposits form on the components and, as we know, present seriousdifficulties in operation. It has been established that the basic cause of varnish formation is the quality of the lubricating oil in the majority of cases. Other factors also influence varnish fo-

mation in an engine.

It follows from the studies of Bouman [30], Gruse and Livingston [31], Mougey [32] and Kadmer [33] that varnishing depends on fuel quality under certain conditions.

Zuidema [34] notes in her book that diesels and spark-ignited engines frequently operate under conditions corresponding to a moderate set of temperature conditions. Under these conditions, the fuel rather than the oil is the principal source of tar and varnish formation. The influence of the fuel on varnish formation in spark-ignited engines is now a generally acknowledged fact.

In recent years, in connection with the appearance of new modifications to internal-combustion engines and the increased demand for catalytic-cracking and sulfurous fuels, it is necessary to devote special attention to the varnishing properties of the fuels.

The varnishing ability of a fuel is manifested when the thin layer of fuel comes into contact with a hot metallic surface. Knowledge of this property is important not only for fuels intended for internal-combustion engines, but also in all cases where fuel comes into contact with heated surfaces.

The varnishing abilities of fuels have been studied by the following procedure [35].

Three cups 27 mm in diameter, 15 mm high at the rim, and containing the fuel to be tested were placed on an interchangeable disk 70 or 100 mm in diameter that had been heated to the specified temperature in a standard varnish former (GOST 5737-53) (Fig. 71).

The fuel to be tested was poured into the ready-weighed cups in the following quantities: 1 ml of diesel fuel, 2 ml of kerosene and 4 ml of gasoline in each cup.

The cups with the fuel were kept in the varnish former until the

fuel had evaporated completely, after which they were removed from the disk, cooled, and weighed. After weighing, the cups were again placed in the varnish former at the temperature of the experiment, held there for 5 min, and then reweighed after cooling. This 5-minute heating operation was repeated (usually 2 – 3 times) until the disagreement in the averaged weight figures of the cups did not exceed 0.5 mg between two successive weighings. The arithmetic mean value over three or two cups, as obtained in the last determination and referred to 10 ml of fuel, was taken as the result of the experiment. The maximum weight discrepancy between cups in a single experiment in which as much as 10 mg of varnish was obtained did not exceed 1 mg, or 2 mg when more than 10 mg of varnish was produced.

The varnishing ability of the tested fuel was computed as the arithmetic mean of two parallel determinations. The disagreement between two parallel determinations did not exceed 2 mg.

The investigations conducted by K.K. Papok and K.I. Bessmertnyy showed that the varnishing ability of fuels depends on their fractional and chemical composition and may be affected when additives are used.

Influence of Fractional Composition on Varnishing Ability of Fuels

The influence of fuel fractional composition on varnishing ability is clearly evident in the example furnished by the products of direct distillation of petroleum: gasolines produced the smallest quantities of varnish, kerosenes are more strongly inclined to form varnish, and diesel fuels form the largest quantities of varnish (in mg per 10 ml of fuel).

| | |
|---|---|
| A-56 automobile gasoline | 6.0 |
| A-66 " " | 9.0 |
| A-70 " " | 1.0 |
| TS-1 fuel | 5.0 |
| T-1 " | 10 |

| | |
|---|---|
| DA diesel fuel | 12 |
| DZ " " | 60 |
| DL " " (S = 1.24%) | 100 |
| Solar oil from Surakhany select petroleum | 116 |
| Solar oil from Balakhany oil petroleum | 245 |

TABLE 32

Physicochemical Properties of Diesel Fuels

| 1 Топливо | 2 Плотность $\rho_4^{20}$ | 3 Вязкость $\nu_{20}$, сст | 4 Сера, % | 5 Фракционный состав | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 6 н. к. | 10% | 50% | 90% | 96% | 7 до 300 | 8 до 350 | 9 к. к. | 10 лак, мг на 10 мл топлива |
| 11 Дизельное топливо: | | | | | | | | | | | | |
| 12 НКЗ (каталитического крекинга), образец № 1 | 0,847 | 4,35 | 0,9 | 220 | 242 | 265 | 316 | 344 | 83,5 | — | — | 65 |
| 13 НКЗ (каталитического крекинга), образец № 2 | 0,877 | 4,5 | 1,25 | 220 | 238 | 266 | 320 | 347 | 80 | — | — | 65 |
| 14 образец № 3 | 0,846 | 5,2 | 1,4 | 173 | 226 | 275 | 331 | 360 | — | 93,5 | — | 104 |
| 15 НКЗ, образец № 4 | 0,852 | 7,4 | — | 225 | 248 | 296 | 363 | — | — | — | — | 143 |
| 16 образец № 5 | 0,845 | 6,12 | 1,18 | 185 | 230 | 280 | 339 80% | — | — | — | 360 | 120 |
| 17 несернистое | 0,868 | 2,39 | 0,3 | 151 | 179 | 216 | 289 | 321 | — | — | — | 23 |
| 18 ДС (ГОСТ 4749-49) | 0,730 | 5,82 | 0,24 | 230 | 250 | 276 | 318 | 334 | 77,5 | — | — | 60 |
| Соляровое масло: 19 | | | | | | | | 93% | | | | |
| 20 из сураханской отборной нефти | 0,841 | 5,24 | — | 187 | 220 | 270 | 350 | 365 | — | — | — | 116 |
| 21 из масляной балаханской нефти | 0,885 | 27,74 | — | 300 | 307 | 332 | 84,5 365 | — | — | — | — | 245 |

1) Fuel; 2) density, $\rho_4^{20}$; 3) viscosity $\nu_{20}$, centistokes; 4) sulfur, %; 5) fractional composition; 6) initial boiling; 7) below 300; 8) below 350; 9) final boiling; 10) varnish, mg per 10 ml of fuel; 11) diesel fuel; 12) NKZ (catalytic cracking), specimen No. 1; 13) NKZ (catalytic cracking), specimen No. 2; 14) specimen No. 3; 15) NKZ, specimen No. 4; 16) specimen No. 5; 17) sulfur-free; 18) DS (GOST 4749-49); 19) solar oil; 20) from Surakhany select petroleum; 21) from Balakhany oil petroleum.

The influence of fractional composition on varnish formation came most clearly to the fore in the test of the 20-degree fractions of various diesel fuels, the physicochemical properties of which are listed in Table 32. The fuels were subjected to distillation in accordance with GOST 1529-42.

As the fractions become heavier, their varnishing ability rises sharply (Fig. 72). The residual fractions have a particularly strong tendency to form varnish. From this we may conclude that as the fractional compositions of the fuels become lighter, their tendency to form varnish deposits will diminish.

Influence of Chemical Composition on Varnish-Forming Ability of Fuels

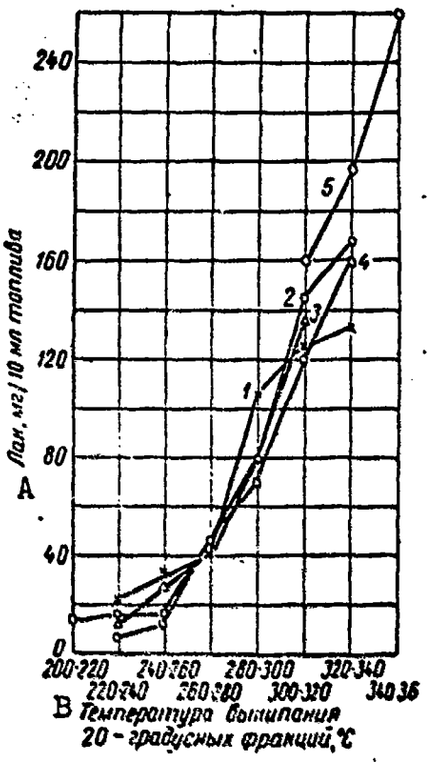


Fig. 72. Varnishing ability of 20-degree fractions of diesel fuels. 1) Diesel fuel NKZ (S = 0.9%); 2) diesel fuel NKZ (S = 1.25%); 3) DS diesel fuel; 4) solar oil from Surakhany select petroleum; 5) solar oil from Balakhany oil petroleum. A) Varnish, mg/10 ml of fuel; B) distillation temperatures of 20-degree fractions, °C.

DS diesel fuel (start of boiling 238°; 90% at 317°) is somewhat heavier in fractional composition than polyalkylbenzene (start of boiling 152°; 90% at 315°) but in spite of this polyalkylbenzene has a varnish-forming ability several times as great. For example, the varnish-forming ability of polyalkylbenzene is 300 mg at 250°, while that of diesel fuel is 60 mg.

This fact indicates beyond question that the influence of chemical composition on varnish formation is being manifested in this case. The dependence of varnish formation on fuel chemical composition has also been confirmed in other experiments.

It was found in an investigation of various groups of hydrocarbons isolated chromatographically by M.S. Borova from diesel fuel L and Baku catalytic gas oil that the aromatic fractions possess stronger varnishing abilities than do the paraffinic-naphthenic fractions (Fig. 73).

It is necessary to remember that the varnishing ability of a fuel

does not necessarily parallel its scaling properties, which are manifested when the fuel burns. A fuel that is stable to oxidation in a thin film may be inclined to form a large quantity of scale on combustion and, conversely, a fuel that is not dangerous from the standpoint of scaling may be extremely dangerous as regards varnish formation.

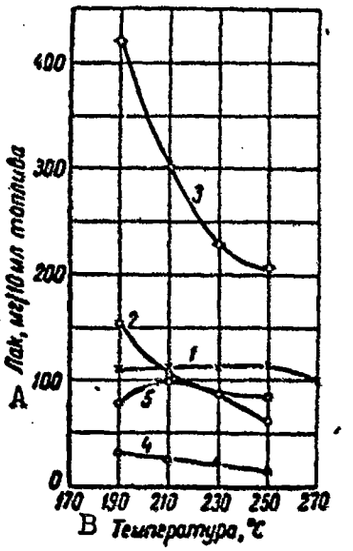


Fig. 73. Varnishing abilities of various groups of hydrocarbons. 1) Diesel fuel L (GOST 305-42); 2) paraffinic-naphthenic fraction of diesel fuel L; 3) aromatic (heptane) fraction of diesel fuel; 4) paraffinic-naphthenic fraction of Baku catalytic gas oil; 5) aromatic (heptane) fraction of diesel fuel. A) Varnish, mg/10 ml of fuel; B) temperature, °C.

We may refer to the following data for an example. It is known that α-methylnaphthalene forms more scale on combustion than does cetane, so that the scaling ability of the mixture increases with increasing content of α-methylnaphthalene in it.

As regards varnish formation, however, we observe the converse relationship: with increasing content of α-methylnaphthalene in mixture with cetane, the varnishing ability of the mixture diminishes. Consequently, when the fuel is oxidized in a thin film, the cetane will represent a greater danger as regards varnish formation than will the α-methylnaphthalene.

Influence of Additives on Varnish-Forming Ability of Fuels

Varnish-formation curves were recorded for two diesel fuels with sulfur contents of 1.18% and 0.3% without additives and with FCh-16 additive in the temperature range from 170 to 250°. The physicochemical properties of the fuels (specimen No. 5 and a specimen of sulfur-free diesel fuel) are listed in Table 31. The FCh-16 additive, which is composed of phenols extracted from semicoking products of

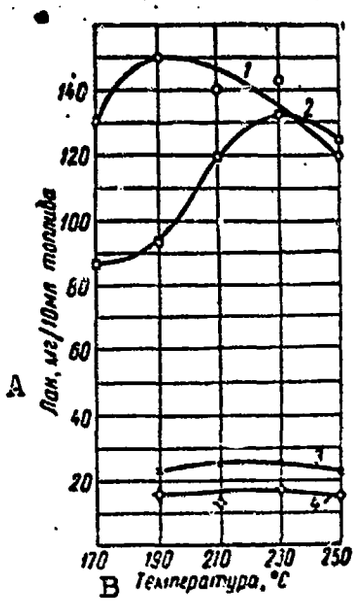


Fig. 74. Variation of varnish-forming ability of fuel on addition of FCh-16 additive. 1) Diesel fuel (S = 1.18%); 2) same + 0.05% of FCh-16 additive; 3) diesel fuel (S = = 0.3%); 4) same + 0.05% of FCh-16 additive. A) Varnish, mg/10 ml of fuel; B) temperature, °C.

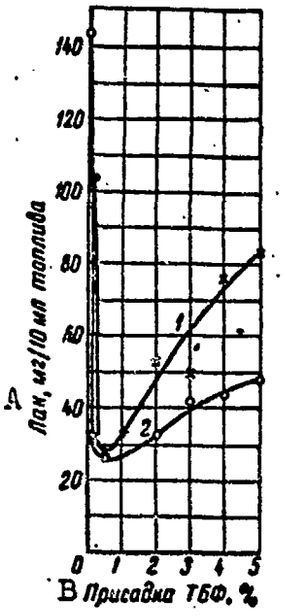


Fig. 75. Varnishing ability of fuel with tributyl phosphate additive. 1) Diesel fuel (S = 1.4%) + TBF additive; 2) NKZ diesel fuel + TBF additive. A) Varnish, mg/10 ml of fuel; B) TBF additive, %.

coals, is used as an antioxidant for various fuels.

Use of the FCh-16 additive with either sulfur-containing or sulfur-free fuel reduced the varnishing ability of the fuels; here, varnish formation was reduced in the temperature range from 170 to 210° for the sulfur-containing fuel, the additive showed little effect above 210°, and the sulfur-free fuel responded less strongly to the additive. In this case, however, varnish formation was reduced over a wider temperature range – namely from 190 to 250° (Fig. 74).

The additive tributyl phosphite [sic] was found particularly effective; on addition of 0.1 to 0.5% of this material to sulfur-con-

taining fuels, their tendency to form varnish dropped sharply (from 104 – 143 to 26 – 28 mg/100 ml of fuel). On a further increase in the additive concentration in the fuel, the quantity of varnish begins to increase (Fig. 75), but even at a 5% additive concentration it is still far below its original value.

It must be remembered that although tributyl phosphite is a useful additive as regards reduction of varnish formation, it is extremely dangerous in large concentrations from the standpoint of scaling.

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## Chapter 9

## NONHYDROCARBON ADMIXTURES IN PETROLEUM AND PETROLEUM PRODUCTS

### NONHYDROCARBON ADMIXTURES IN PETROLEUM

Depending on the petroleum deposit, the refining methods, and the conditions of storage and utilization, various quantities of nonhydrocarbon admixtures can be detected in the composition of petroleum products. In general, the quantity of such admixtures is not great. However, with the continuous improvement in engines and fuel equipment, these admixtures have an ever increasing negative effect on the quality of the fuels and oils (lubricants). On the other hand, certain nonhydrocarbon admixtures in petroleum and petroleum products can serve as a great source of new chemical compounds that has not been used to the present time, and these compounds, if extracted, would doubtlessly play an important role in the national economy.

All of the nonhydrocarbon admixtures detected in petroleum products can be divided into the four major groups:

1) sulfur compounds;

2) nitrogen compounds;

3) oxygen compounds;

4) admixtures containing "ash" elements.

Sulfur and nitrogen compounds are carried into fuels and oils from a petroleum subject to conversion as a result of the refining techniques employed. The occurrence of such compounds is not uniform in the hydrocarbon fractions. They are predominantly concentrated in the high-boiling and residue products.

This same relationship exists for oxygen compounds, with the exception that the content of such compounds may increase noticeably as a result of the oxidation (by the oxygen in the air) of the less stable components of the petroleum products during their production, storage, and utilization.

The unstable components include not only a certain group of the hydrocarbons whose tendency to oxidation is great, but certain nonhydrocarbon compounds as well: sulfur, nitrogen, and oxygen compounds. The capacity of the majority of these compounds to react, their tendency to oxidation, as well as their tendency to consolidation or as is sometimes said, resinification, is great.

Consequently, the initial content in the petroleum products of sulfur and nitrogen compounds will not increase, whereas under certain temperature conditions the quantity of these compounds may diminish as a result of the conversions which take place with the liberation of volatile compounds. The quantity of oxygen compounds can increase through formation.

The admixtures containing "ash" elements will be composed of the products of the corrosion of equipment, tanks, the metals of the engine fuel system, and the contamination which penetrates the petroleum products during the processes of storage, transportation, and utilization. Compounds with "ash" elements contained in the initial petroleum are concentrated almost entirely in the residue products (mazout, "gudron" [petroleum asphalt], and bitumen). The quantity of volatile compounds with "ash" elements is negligible.

In the more typical petroleums, we generally find the following in the form of nonhydrocarbon admixtures (in %):

| | |
|---|---|
| sulfur . . . . . | 0.05-5.0 |
| nitrogen . . . . . | 0-1.0 |
| oxygen . . . . . | 0.1-5.0 |
| ash . . . . . | 0.002-0.038 |

TABLE 33

Content of Sulfur, Nitrogen, and Oxygen in Petroleum-Refining Products

| 1 Фракции | 2 Средний молекулярный вес | 3 Содержание, % | | |
|---|---|---|---|---|
| | | S | N | O |
| 4 До 200° | 150—200 | 0,02—0,50 | 6 Следы | Следы |
| 200—350° | 200—250 | 0,04—1,50 | 0,01—0,2 | 0,01—0,5 |
| 5 Выше 325° | 250—400 | 0,30—4,0 | 0,05—0,4 | 0,7—1,5 |

1) Fraction; 2) mean molecular weight; 3) content, %; 4) below 200°; 5) above 325°; 6) traces.

Depending on the geological conditions of petroleum formation, the content of nonhydrocarbon admixtures may vary markedly.

The molecular weight of sulfur-, nitrogen-, and oxygen-bearing compounds is generally close to the molecular weight of the hydrocarbons which they accompany. In terms of structural variety, they are on a par with the hydrocarbon mixtures. The multiplicity of these compounds and the similarity in structure between the hydrocarbon radicals to the structure of the basic hydrocarbon composition of petroleum products serve as an explanation for the difficulties which arise in separating the nonhydrocarbon admixtures (particularly the sulfur and nitrogen compounds) from the basic hydrocarbon portion of fuels or oils. At the present time, particular attention is being devoted to the development of efficient separation methods.

We can judge as to the manner in which the nonhydrocarbon admixtures are distributed in the petroleum-refining products by examining the limits of sulfur, nitrogen, and oxygen content presented in Table 33.

We can form an opinion as to the content of nonhydrocarbon admixtures in petroleum-refining products on the basis of the following calculation.

In a contemporary petroleum diesel fuel in which a sulfur content

of up to 1% is tolerated, some 7.5% will be made up of sulfur compounds having the same molecular weight as the hydrocarbons in the fuel, with only a single sulfur atom per molecule. In this same fuel, given the earlier conditions and an oxygen content of 0.5%, there will be more than 3% of oxygen compounds; given a nitrogen content of 0.2%, there will be some 1.5% nitrogen compounds. Consequently, a standard diesel fuel will contain some 12% nonhydrocarbon admixtures, not counting the compounds with the "ash" elements.

NONHYDROCARBON ADMIXTURES IN VARIOUS FUELS

Let us examine in general form the distribution and composition of the nonhydrocarbon admixtures in the petroleum-refining products.

Table 34 shows the content of sulfur in the distillates obtained from certain sulfur and low-sulfur petroleums.

It is assumed that in the gasoline and ligroin direct-distillation distillates, the hydrocarbon radicals of the sulfur compounds have a predominantly aliphatic structure. Radicals of cyclic structure predominate in thermal-cracking and high-boiling direct-distillation fractions. In this connection, the aromatic portion of the distillates of many petroleums contains the basic quantity of sulfur compounds and it can therefore be designated, with full justification, as a sulfur concentrate.

The data presented in Table 35 illustrate well what has been stated above.

Satisfactory gasolines and ligroins can be obtained from the greater part of the high-sulfur-bearing petroleums. Kerosenes and diesel fuels, satisfying the sulfur-content standards, are adequate without additional purification only in the case of low-sulfur-bearing petroleums.

As an example, Table 36 shows data on the maximum permissible sulfur content in petroleums for the derivation of commercial products meeting specifications. It is easy to see that in terms of sulfur con-

TABLE 34

Distribution of Sulfur in Petroleum-Refining Products [1, 2]

| 1 Нефти | | 2 Содержание серы (в % вес.) во фракции с температурой кипения, °С | | | |
|---|---|---|---|---|---|
| 3 Месторождение | 4 содержание серы, % вес. | 13 до 200 | 150—300 | 200—350 | 14 выше 300 |
| 5 *Сернистые* | | | | | |
| 6 Ишимбаевское | 2,17—4,32 | 0,43—0,95 | 1,07—2,10 | 1,90—2,05 | 2,85—4,08 |
| 7 Туймазинское | 1,47—3,23 | 0,09—0,32 | 0,72—1,90 | 0,90—2,20 | 2,24 |
| 8 Бугурусланское | 2,70 | 0,58—0,92 | 1,53—1,72 | 2,10 | 3,45—3,77 |
| 9 *Малосернистые* | | | | | |
| 10 Малгобекское | 0,45 | — | 0,065 | 0,109 | 0,60 |
| 11 Апшеронское | 0,22 | 0,004 | 0,006 | 0,032 | 0,27 |
| 12 Грозненское | 0,32 | 0,04 | 0,03 | 0,06 | 0,57 |

1) Petroleum; 2) sulfur content (in % by weight) in the fraction having the following boiling point, °C; 3) deposit; 4) sulfur content, % by weight; 5) sulfur; 6) Ishimbay; 7) Tuymazy; 8) Buguruslan; 9) low in sulfur; 10) Malgobek; 11) Apsheron; 12) Groznyy; 13) below 200; 14) above 300.

TABLE 35.

Content of Sulfur in High-Boiling Fractions of Uzbek Petroleum [3]

| 1 Температура кипения фракций, °С | 2 Содержание серы, % вес. | |
|---|---|---|
| | 3 в исходной фракции | 4 после удаления ароматических углеводородов |
| 300—350 | 4,46 | 0,18 |
| 350—400 | 5,54 | 0 |
| 400—450 | 5,60 | 0 |
| 450—500 | 5,51 | 0 |

1) Boiling point of fractions, °C; 2) sulfur content, % by weight; 3) in initial fraction; 4) after removal of aromatic hydrocarbons.

tent there are various requirements imposed on petroleums, depending on the commercial product to be derived.

The various requirements with respect to the maximum sulfur content in petroleums serve as the index for the derivation of products which

TABLE 36

Maximum Permissible Sulfur Content in Petroleums for Derivation of Commercial Products Meeting Specifications [4]

| 1 Товарные продукты | 2 Нормы содержания серы по спецификациям, % | 3 Допустимое содержание серы в нефтях, % | | |
|---|---|---|---|---|
| | | 4 США | 5 Венесуэлы | 6 Ближнего Востока |
| 7 Авиационный бензин | 0,05 | 1,0 | 2,1 | 2,2 |
| 8 Автомобильный бензин | 0,10 | 1,8 | 2,9 | 3,7 |
| 9 Керосин | 0,13 | 0,5 | 0,54 | 0,62 |
| 10 Дизельное топливо | 0,50 | 1,1 | 1,1 | 0,60 |
| 11 То же | 1,00 | 2,1 | 2,2 | 1,60 |

1) Commercial products; 2) sulfur-content standards, according to specifications, %; 3) permissible sulfur content in petroleums, %; 4) USA; 5) Venezuela; 6) Near (Middle) East; 7) aviation gasoline; 8) automotive gasoline; 9) kerosene; 10) diesel fuel; 11) the same.

correspond to the requirements imposed by the GOST [All-Union State Standards] or specifications and they are functions not only of the sulfur content but of the composition of the sulfur compounds within the petroleums as well. A portion of the sulfur compounds, under the conditions prevailing in petroleum refining, will become subject to destruction with the formation of easily removed gaseous hydrogen sulfide or similar low-molecular compounds. The greater the quantity of stable sulfur compounds in the petroleum, the more extensive their participation in the commercial products.

This study of the individual composition of sulfur compounds is connected with a great many difficulties. Nevertheless, investigations conducted over many years in this area have been crowned with a certain measure of success. At the present time, a great quantity of sulfur compounds is being extracted from and identified in petroleums and petroleum products.

It is somewhat easier to undertake the investigation of the group

composition of sulfur compounds. By group we mean the compounds with hydrocarbon radicals of various structures having a common identical structural sulfur distribution. The group-analysis methods have not yet been fully perfected. They do not exhaust the great variety of accompanying compounds. As a result of such an analysis, there remains a substantial portion of the sulfur compounds which cannot be referred to one of the identified compound groups.

Despite this fact, group analysis of sulfur compounds yields some idea as to the composition of these compounds.

The presence of sulfur, hydrogen sulfide, mercaptans, sulfides, thiophanes, and thiophenes has been firmly established in petroleums and petroleum products.

Elementary sulfur (S). Formed in distillates as a result of the thermal decomposition of sulfur compounds having a more complex structure. Elementary sulfur is extremely corrosive when in contact with copper and its alloys.

Hydrogen sulfide ($H_2S$). May be present in free state in petroleum and it may be formed in the thermal decomposition of more complex sulfur compounds. It is extremely corrosive in contact with ferrous and nonferrous metals, particularly in the case of copper and its alloys. With iron, it forms ferrous sulfide whose conversion products exhibit pyrophoric properties. Commercial products must be completely free of hydrogen sulfide.

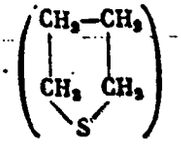
Mercaptans (R - SH). Reaction-capable compounds which tend to oxidation, consolidation, and interaction with nonferrous metals, particularly copper and its alloys, and cadmium. In the presence of the mercaptans, the fuels have an unpleasant odor; the solubility of certain plastic materials increases in such fuels. The activity of the mercaptans varies and is determined by the structure of the hydrocarbon radi...

The content of mercaptans in fuels is strictly limited.

Sulfides (R – S – R'). The reaction capacity and corrosive activity of the sulfides increases with temperature.

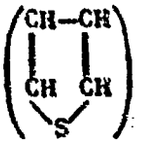
Di- and polysulfides (R – S – S ... – R'). These exhibit a tendency to consolidation with the formation of tars which are separated from the fuel in the form of a second phase. With an increase in temperature, the corrosive activity of these compounds increases.

Thiophanes and their homologs



With an increase in temperature, given the catalytic influence of metals, particularly of copper and its alloys, these compounds are subject to extensive conversion with the formation of tarry (resinous) substances.

Thiophene and its homologs



are included among the most inert and stable sulfur compounds.

Table 37 shows the group composition of sulfur compounds in commercial fuels boiling within the ligroin-kerosene-fraction range.

The data in the table do not provide a complete picture of the chemical structure of all the sulfur compounds. Unsaturated sulfur compounds may exist in the fuels, as may certain of their oxides and, possibly, extremely high-reaction-capacity structures which will also participate in the formation of consolidation products in the fuels and intensify the corrosive activity of the compounds.

Nitrogen compounds can be detected in substantially smaller quan-

TABLE 37

Composition of Sulfur Compounds in Fuels [5]

| 1 Показатели | 2 Прямая перегонка | | | | 3 Термический крекинг | | |
|---|---|---|---|---|---|---|---|
| | I | II | III | IV | I | II | III |
| 4 Содержание серы в топливах, % | 0,123 | 0,219 | 0,220 | 0,178 | 0,941 | 0,647 | 0,506 |
| 5 *Состав сернистых соединений, %* | | | | | | | |
| 6 Меркаптаны | 3,26 | 18,53 | 23,63 | 12,35 | 0,67 | 9,57 | 1,18 |
| 7 Сульфиды: | | | | | | | |
| 8 алифатические | 51,10 | 47,50 | 26,50 | 63,00 | 14,25 | 32,60 | 13,60 |
| 9 ароматические | 8,15 | Нет | 7,08 | 8,97 | 31,20 | 40,80 | 35,20 |
| 10 Дисульфиды | 2,97 | 14,80 | 9,74 | 14,00 | Нет | 8,10 | 0,26 |
| 11 извлекаемые ртутью | 4,72 | 9,20 | 15,98 | 1,68 | 2,66 | 0,83 | 7,70 |
| 12 В том числе: | | | | | 15 | | |
| 13 элементарная сера | 2,38 | 2,96 | 0,20 | 1,68 | Не определялась | | |
| 14 Неопределяемая сера | 29,80 | 9,97 | 17,07 | Нет 16 | 51,22 | 7,90 | 42,06 |
| 17 Всего | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

1) Indicator; 2) direct distillation; 3) thermal cracking; 4) sulfur content in fuels, %; 5) composition of sulfur compounds, %; 6) mercaptans; 7) sulfides; 8) aliphatic; 9) aromatic; 10) disulfides; 11) extracted by means of mercury; 12) including; 13) elementary sulfur; 14) undetermined sulfur; 15) not determined; 16) none; 17) total.

tities than sulfur compounds in petroleums. It may be for this reason that these nitrogen compounds became of interest only in recent times, in connection with the development of catalytic processes of petroleum refining and as a result of the increased requirements imposed on petroleum-product stability. It has been established that the nitrogen compounds in petroleum reduce the activity of the catalysts and intensify the resinification of the petroleum products.

Neutral and basic nitrogen compounds can be distinguished in petroleum and in petroleum products. Basic among these are the nitrogen compounds which can be extracted by acid-solution processing. The portion of the compounds that cannot be extracted in this manner are classified as neutral.

In this case, the basicity of the nitrogen compounds does not correspond to a rigorous chemical concept, since the thoroughness of their interaction with the acid may vary as a function of the chemical structure of the molecules.

In the light petroleum fractions there are no nitrogen compounds or they can be detected only in negligible quantities. With an increase in the boiling point of the fractions the nitrogen-compound content increases. For example, in the fractions of the sulfur-bearing Romashkin petroleum, said fractions boiling over in a range from 300 to 350°, the quantity of nitrogen amounted to 0.03%; in the range between 350 and 550° and above 550° the nitrogen content was, respectively, 0.05% and 0.25%; in the tars the nitrogen content came to 0.64%. The fraction of the basic nitrogen with respect to the total nitrogen in the petroleum amounted to 28%, and in the fractions boiling over within a range of 175 to 300°, 300-350°, and 350-550°, the ratio between the basic nitrogen and the total nitrogen in the petroleum amounted to, respectively, 100%, 83%, and 70%; in the fraction boiling over above 550°, this ratio amounted to 30%, and it was 24% in the tars [6].

There are many data which confirm the nonuniform distribution of nitrogen compounds in petroleum-refining products. It was established that with an over-all content of nitrogen in the Dagestan petroleums of 0.14-0.16%, 26% of nitrogen remains in the oil fractions, and 60% of nitrogen remains in the tars removed with silica gel; 14% of nitrogen remains in the asphaltenes.

The mixture of nitrogen compounds evolved from these petroleums exhibited the following characteristic [7].

| | |
|---|---|
| Specific weight | 1.0241 |
| Molecular weight | 250 |
| Refractive index $n_D^{20}$ | 1.5528 |
| Boiling point, °C | 326 - 340 |

Elementary composition, %:

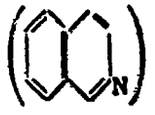
| | |
|---|---|
| C | 82.92 |
| H | 9.61 |
| O | 1.47 |
| N | 5.23 |
| S | 0.77 |

The presence of sulfur and oxygen should be attributed to the accompanying admixtures in sulfur and oxygen compounds.

Primarily three groups of basic nitrogen compounds can be distinguished in petroleum products.

I. Pyridine derivatives

II. Quinoline derivatives

III. Isoquiline derivatives 

The presence of small quantities of aromatic amines is possible. Aliphatic amines have not been found.

Some 85 individual nitrogen compounds, basic in nature [8], have been extracted from petroleums to the present time. Nonbasic compounds have not been thoroughly studied. Hypothetically, these include primarily the derivatives of pyrrole

and the nitriles (compounds containing the cyanide group, C ≡ N) etc.

Most of the nitrogen compounds are thermally stable. For example, quinoline is subject to condensation with the breaking of the ring only at 500°, and here a heavy residue is formed. The isoquinoline also reacted, but somewhat more rapidly [9].

Their derivatives, depending on the structure, possibly may react at an even lower temperature; however, for us it is important that this process take place with a formation of a new and more consolidated molecule.

Oxygen compounds of petroleum products have not been studied to any great extent, although their quantity may increase and attain considerable magnitudes, depending on the various factors involved. These factors include: 1) the compounds that are present in the initial crude (raw material); 2) the compounds newly formed in the refining of the petroleum; 3) the products of the oxidation of the hydrocarbon and nonhydrocarbon portions of the commercial product under conditions of storage and utilization.

Oxygen compounds should also be distinguished in terms of the extent of the oxidation conversions as a result of which they were formed.

As is well known, the oxidation of organic compounds in the liquid phase involves a multistage process and these processes develop in accordance with the laws governing branched and degenerate chain reactions. As a result of the fact that in a hydrocarbon medium a substantial quantity of oxygen compounds may exist – the products of the subsequent conversions, beginning with the primary structures having a molecular weight close to the compound being oxidized, all the way to the final structures that do not experience change under the given conditions.

The simplest initial products of the oxidation will easily be distilled with the petroleum fractions, spreading among these. The most complex final products of the oxidation and their consolidation will be characterized by a high molecular weight and in the distillation of the petroleum fractions they will be concentrated in the residue.

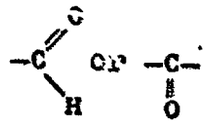
It can be assumed that in the sequence of oxidization conversions,

the following groups of oxygen compounds are formed.

1. Peroxides of the ROOH or ROOR' type, present in extremely small quantities; these are subject to further conversions.

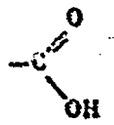
2. Alcohols and phenols, characterized by the OH group. These compounds are quite stable and will represent a substantial portion of the formed oxygen compounds.

3. Compounds with the carbonyl group



This is a small quantity. In terms of their chemical nature, they tend under certain conditions to further conversions: condensation, polymerization, and oxidation.

4. Acids characterized by the following group:



Most frequently the quantity of these does not exceed 2-5% of the entire quantity of oxygen compounds. Acids are extremely stable at comparatively high temperatures. They are regarded as corrosively aggressive. However, this is valid only for compounds of low molecular weight. The higher the molecular weight of the acids, the lower their corrosive activity.

It should be stressed that the acidity of the petroleum products does not offer any idea as to the entire quantity of oxygen compounds contained in petroleums and in the products of petroleum refining.

5. Semifunctional oxygen compounds (oxy acids, keto acids and formaldehydes), condensation products (esters), and polymerization and consolidation products of different types. All of these compounds appear as a result of side processes which develop during oxidation, and whose in-

tensity is determined by the chemical structure of the material being oxidized, the temperature conditions, and the time and catalytic activity of the metals in contact with the fuel or oil.

Oxidation products may also be present, and these are characterized by two identical functional groups such as, for example, peroxides, alcohols, phenols, acids, etc.

With the development of the chromatography method, it became possible to separate oxygen compounds from the hydrocarbon mixture. The investigation of oxygen compounds in commercial fuels, boiling over within the range of the ligroin-kerosene fractions, demonstrated that 75-85% of the entire quantity of oxygen compounds is distilled in a vacuum. The overwhelming part of the oxygen compounds is characterized by the hydroxyl groups (alcohols and phenols) and has the structure of an aromatic ring with side unsaturated chains [10].

Hence it follows that the least stable hydrocarbons of these fractions, subject to oxidation at the temperature of the ambient air, are the olefinic-aromatic hydrocarbons. These underwent oxidation with the unsaturated bonds preserved.

Aliphatic-structure compounds with two or more unsaturated bonds and to some extent the unsaturated naphthenes should be included among the extremely unstable hydrocarbons that exhibit tendency to oxidation under the "soft" conditions which may possibly prevail in contemporary commercial petroleum products.

The fourth group of nonhydrocarbon admixtures includes the compounds with "ash" elements.

The presence of admixtures cannot be tolerated in fuels nor in oils. Consequently, we are dealing here with microquantities of these compounds whose presence cannot be established in the form of a second solid phase detectible to the naked eye in ordinary light.

At the same time, these quantities, as will be demonstrated in the following chapter, may produce negative consequences under the conditions prevailing in the utilization of petroleum products. The basic mass of mineral admixtures in petroleum is concentrated in the residue products as the petroleum is refined. For example, research in the mazouts of numerous petroleums has shown that the concentration of oxides and sulfur in the "ash" portion of the mazouts varied within the following range (in % x $10^{-4}$) [11].

| | |
|---|---|
| $Na_2O$ | 2 - 320 |
| $V_2O_5$ | 2 - 550 |
| CaO | 0 - 250 |
| NiO | 0 - 300 |
| MgO | 0 - 30 |
| $Fe_2O_3$ | 2 - 350 |
| $SiO_2$ | 0 - 275 |
| $Al_2O_3$ | 0 - 50 |
| $P_2O_5$ | 0 - 15 |
| Sulfates | 0 - 450 |
| Sulfur | 5000 - 30000 |

It is assumed that such elements as Al, Ca, Mg, Si, and Na are present as complexes or salts in the form of suspensions or solutions in water; Fe, Ni, and V are possible in the form of porphyrinic complexes in the petroleum.

In order of diminishing petroleum ash content, the elements can be classified as follows [12]: S, O, P, N, V, K, Ni, Si, Ca, Fe, Mg, Na, Al, Mn, Pb, Ag, Au, Cu, U, Ti, Sn, and As.

Hence we can see that a substantial portion of the sulfur and oxygen in the petroleum products can be presented in the form of a compound with the "ash" elements.

The prevention of the corrosion activity of the residual fuels is a function not only of the existing sulfur, but also of the detected compounds in the ash: $Na_2SO_4$ (... $SO_2$, ... $SO_3$, ... $O_2$), $NaVO_3$, the complex

$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$, of oxygen, $V_2O_5$, and of the system $Na_2SO_4 - V_2O_5$, and it – the prevention of the corrosion activity– presents a serious problem to whose solution much effort is being devoted [13].

However the negative role of the ash elements is not limited to their corrosion activity. By means of radioactive tracers it has been established that after the distillate diesel fuel has been replaced with heavy fuel (containing the residual products of petroleum refining), the abrasive properties of the spent oils (lubricants) increased as did the wear on the cylinder casings [14].

Compounds with ash elements accumulate in the distillate products of petroleum refining as a result of the corrosive dissolution of the tanks, the tubing, the pumping facilities, and the fuel systems of the engines. Moreover, dust from the atmosphere and mineral impurities of water will penetrate into the fuels and oils in the presence of water. In this connection, the composition of the ash elements varies.

As an example let us cite the composition of the ash contained in the TC-1 fuel that is subjected to hydraulic purification. The quantity of ash that remains after the combustion of such a fuel is not very great, amounting to 0.85 mg/l as against the completely acceptable quantity 0.005%, or about 40 mg/l (GOST 4138-49).

A spectral analysis of this ash showed the presence of 3.0% Na, 2.5% Al, 6.5% Fe, 10.0% Ca, 11.0% Mg, 12.5% Si, 2.0% Zn, 2.5% Pb, and other elements as well. It is quite clear that this ash composition is determined by the products of the corrosion of the metals and the contamination that penetrates into the fuel from without.

The removal of these impurities is possible by the fine filtration of the petroleum products.

However, the removal by filtration of particles having dimensions of 1-30 μ is an extremely difficult problem. In the literature, we can

encounter statements to the effect that it is necessary for this purpose to employ electric filters [15].

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## Chapter 10

## TARS AND SLUDGE FORMATION IN HYDROCARBON MIXTURES

### TARS

Under the conditions of prolonged storage, many fuels give trouble in the form of excessively rapid tarring. In this process, the bulk products acquire a dark coloration and viscous tars that are extremely difficult to remove fall to the bottom of the tank. In the engine's [fuel] system, under the influence of high temperature and the catalytic action of the metals, fuels and oils that are inclined to oxidize precipitate tarry substances that plug filters, fuel and oil lines, and precision-fitted working pairs, interfering with normal fuel supply to the engine and normal operation of the fuel system. The processes that unfold at higher temperatures are accompanied by the formation of a solid phase – sludge, which has an even more detrimental effect on normal engine operation.

Certain fuel and oil components may produce deposits of varnish – solid products of profound thermal transformations – on the engine's cylinder-and-piston group.

An investigation of the elementary composition of the tars, sludges and varnishes showed that these substances consist of carbon, hydrogen, large quantities of oxygen, sulfur, nitrogen and mineral elements. Subsequently, the nonhydrocarbon impurities present and forming in fuels and oils are the initial materials that determine the accumulation of tars, sludges, varnishes and other nonhydrocarbon condensation products.

Tars are high-molecular-weight products of oxidative transformations and condensation of unstable hydrocarbons and nonhydrocarbon impurities in fuels and oils.

Let us examine the composition and conditions of formation of tars as primary products in this complex chain of transformations.

The quantity of tars is judged from the sum of the compounds that separate from the hydrocarbon mixture onto an active adsorbent as a result of their higher polarity. The mixture of nonhydrocarbon compounds that has been separated chromatographically consists of the sum total of the oxygen compounds that had been present in the petroleum products and some of the sulfur and nitrogen compounds.

TABLE 38

Characteristics of Tar Composition in Petroleum and Its Fractions

| 1 Продукты | 2 Состав, % | | | | 3 Молекулярный вес | 4 Формула | 5 Гомологический ряд |
|---|---|---|---|---|---|---|---|
| | C | H | S | O | | | |
| 6 Исходная нефть | 84,4 | 9,77 | 0,79 | 5,30 | 585 | $C_{41}H_{69}O_2$ | $C_nH_{2n-24}O_2$ |
| 7 Керосин . . . . | 77,90 | 9,97 | 1,80 | 10,33 | 290 | $C_{19}H_{39}O_2$ | $C_nH_{2n-10}O_2$ |
| 8 Газойль . . . . . | 80,92 | 9,92 | 1,56 | 7,60 | 319 | $C_{22}H_{31}O_2$ | $C_nH_{2n-12}O_2$ |
| 9 Не вязкий дистиллят . . . . | 82,29 | 10,22 | 1,26 | 6,23 | 466 | $C_{32}H_{47}O_2$ | $C_nH_{2n-16}O_2$ |
| 10 Вязкий дистиллят | 82,62 | 10,00 | 1,17 | 6,15 | 471 | $C_{32}H_{47}O_2$ | $C_nH_{2n-16}O_2$ |
| 11 Остаток. . . . . | 84,75 | 9,75 | 0,51 | 4,92 | 757 | $C_{53}H_{73}O_2$ | $C_nH_{2n-32}O_2$ |

1) Products; 2) composition, %; 3) molecular weight; 4) formula; 5) homologous series; 6) starting petroleum; 7) kerosene; 8) gas oil; 9) low-viscosity distillate; 10) viscous distillate; 11) residue.

In petroleums, the total amount of compounds that separate out onto the silica gel or, as they are normally called, "silica-gel" tars, varies between 2 and 53% [1, 2]. On the average, this quantity is 15% for typical petroleums of the Soviet Union.

With increasing molecular weight of the tars, the cyclization observed in their molecules increases. It is assumed that in this case,

TABLE 39

Silica-Gel Tars of Cracking Kerosenes

| 1 Показатели | 2 Крекинг-керосин из нефтей Башкирской АССР | | 5 Крекинг-керосин из нефтей Татарской АССР | | 6 Крекинг-керосин из бакинских нефтей | |
|---|---|---|---|---|---|---|
| | 3 исходный | 4 после перколяции через силикагель | 3 исходный | 4 после перколяции через силикагель | 3 исходный | 4 после перколяции через силикагель |
| 7 Количество смол в крекинг-керосине после 18 месяцев хранения, мг/100 мл | 670 | 2520 | 533 | 2400 | 1805 | 8080 |
| 8 *Характеристика смол* | | | | | | |
| 9 Удельный вес $d_4^{20}$ | 1,037 | 1,030 | 0,9727 | 1,0345 | 1,0490 | 1,0444 |
| 10 Молекулярный вес | 218 | 261 | 183 | 266 | 238 | 251 |
| 11 Йодное число | 75 | 54 | 146 | 54 | 130 | 50 |
| 12 Коэффициент рефракции $n_D^{20}$ | 1,5372 | 1,5220 | 1,5281 | 1,5385 | 1,5300 | 1,5330 |
| 13 Гидроксильное число, мг КОН/г | 100 | 126 | 172 | 83 | 127 | 87 |
| 14 Кислотное число, мг КОН/г | 12 | 14 | 2 | 17 | 6 | 11 |
| 15 Эфирное число, мг КОН/г | 23 | 49 | 10 | 66 | 34 | 51 |
| 16 Карбонильное число, мг $O_2$/г | 7 | 24 | 0 | 13 | 0 | 10 |
| 17 Содержание серы, % | 4,9 | 2,8 | 6,7 | 2,4 | 1,25 | 0,30 |
| 18 Пределы кипения при 5 мм рт. ст., °С | 60—150 | 45—125 | 66—140 | 56—110 | 70—150 | 60—125 |
| 19 Выход перегоняющихся соединений, % | 70 | 65 | 73 | 70 | 78 | 75 |

1) Index; 2) cracking kerosene from petroleums of Bashkirskaya ASSR; 3) initial; 4) after percolation through silica gel; 5) cracking kerosene from petroleums of Tatarskaya ASSR; 6) cracking kerosene from Baku petroleums; 7) quantity of tars in cracking kerosene after 18 months of storage, mg/100 ml; 8) description of tars; 9) specific gravity $d_4^{20}$; 10) molecular weight; 11) iodine number; 12) refractive index $n_D^{20}$; 13) hydroxyl number, mg of KOH/g; 14) acid number, mg of KOH/g; 15) ester number, mg of KOH/g; 16) carbonyl number, mg of $O_2$/g; 17) sulfur content, %; 18) boiling range at 5 mm Hg, °C; 19) distillate yield, %.

aromatic, naphthenic and heterocyclic rings may become joined, either directly or through bridge bonds formed by oxygen, sulfur and nitrogen [3, 4, 5].

The manner in which the elementary composition of tars distri-

buted among the petroleum fractions varies may be judged from the data of A.N. Sakhanen listed in Table 38.

The average molecular weight of the tars increases with increasing molecular weight of the hydrocarbon fractions. If we disregard the small quantity of nitrogen (which is not indicated in the table), then no fewer than two oxygen atoms devolve upon the average tar molecule; this enables us to regard them as a mixture consisting largely of oxygen compounds of structurally similar homologous series.

The basic part of the resins is concentrated in the heavy and residual products.

The tar content and, consequently, the oxygen-compound content in the ligroin-kerosene fractions becomes noticeable. In these direct-distillation fractions, the tar content rises to 0.1 – 0.2%, and to 0.6 – 1.0% in cracking fractions [7]. The quantity of tar increases during prolonged storage of petroleum products under the influence of elevated temperature, catalytically active metals and contact with atmospheric oxygen.

Table 39 [8] gives a conception of the manner in which silica-gel tars may accumulate in fuels during prolonged storage under normal conditions, together with a characterization of the tars.

In cracking kerosenes, which are distinguished by large contents of unstable hydrocarbon and nonhydrocarbon impurities, the quantity of tars detected after deposition of the original tars after 18 months of storage at the ambient temperature was 4 to 5 times the amount found in control fuel specimens from which the resins had not first been separated. This means that oxidation processes in fuels that have been freed of tars, including oxygen-inhibiting compounds, develop at a much greater speed.

The tars were substances with high specific gravities and high

TABLE 40

Elementary Composition of Tars and Their Transformation Products (in %)

| 1 Продукты | C | H | S | N | O | 2 Зола | 3 Сумма зольных элементов |
|---|---|---|---|---|---|---|---|
| 4 Смолы кзыл-тумшукской нефти [11] | 79,48 | 9,00 | 7,81 | 0,83 | 2,40 | 0,48 | — |
| 5 Асфальтены этих смол [11] | 79,43 | 8,99 | 7,85 | 0,85 | 2,49 | 0,39 | — |
| 6 Смолы лигроино-керосиновых фракций прямой перегонки [10] | 72,85—79,25 | 10,85—11,81 | 12,56—11,53 | 0,10—0,67 | 4,10—7,93 | — | — |
| 7 Осадки, полученные при 25° и задержанные на фильтре из сернистой фракции | 13,65 | 4,30 | 4,69 | 1,20 | 41,20 | — | 34,60 |
| 8 То же, полученные при 120° | 8,98 | 2,20 | 10,68 | 0,61 | 28,39 | — | 49,14 |
| 9 Осадки, полученные при 150° и задержанные на фильтре из малосернистой фракции | 11,21 | 4,08 | 9,35 | 0,97 | 49,37 | — | 25,02 |
| 10 Смолы крекинг-керосинов [10] | 75,13—77,41 | 9,33—9,81 | 3,63—5,10 | 1,09—1,23 | 7,55—8,27 | — | — |
| 11 Вязкий осадок, выпавший при хранении крекинг-керосина [11] | 76,10—78,50 | 6,3—6,9 | 7,7—8,7 | 1,8—3,4 | 1,3—4,1 | 0,7—2,5 | — |
| 12 Осадки, полученные при 135° и задержанные на фильтре из малосернистого крекинг-топлива | 55,4 | 6,24 | 2,68 | 2,22 | 21,01 | — | 12,45 |
| 13 Нагары с двигателя М-11 после неэтилированных бензинов [12] | 71,9—75,8 | 4,8—5,2 | 15 По определены | | 16,0—19,6 | 1,4—6,6 | — |
| 14 Лаки, снятые с авиадвигателей после неэтилированных бензинов [12] | 81,0—85,7 | 7,0—9,2 | 16 То же | | 4,8—10,4 | 0,4—2,6 | — |

1) Products; 2) ash; 3) total ash-forming elements; 4) tars of Kzyl-Tumshukskiy petroleum [11]; 5) asphaltenes of these tars [11]; 6) tars of ligroin-kerosene fractions from direct distillation [10]; 7) sediments obtained at 25° from sulfur fraction and trapped on filter; 8) same, obtained at 120°; 9) sediments obtained at 150° from low-sulfur fraction and trapped on filter; 10) cracking-kerosene tars [10]; 11) viscous residue deposited during storage of cracking kerosene [11]; 12) sediments obtained at 135° from low-sulfur cracking fuel and trapped on filter; 13) scale from M-11 engine after [use of] unethylated gasolines [12]; 14) varnishes removed from aviation engines after use of unethylated gasolines [12]; 15) not determined; 16) same.

refractive indices, which testified to the predominance of the aro-

matic structure among them. The oxygen compounds were characterized by various functional groups. However, compounds with hydroxyl groups predominated in the tars; there was a large sulfur content.

It is interesting to note that much sulfur is present in tars from kerosenes produced from low-sulfur Baku petroleums. After separation of the tars that had been present, there was also much sulfur in the new tars that formed, indicating passage of new amounts of the sulfur compounds from the fuels into the tars, possibly after the appropriate oxidative transformations. Perhaps the same observations would have been made for the nitrogen compounds, which were not determined in this case.

The tars, which were extracted chromatographically, were distilled in a vacuum. The distillate yield was 65 - 78%. Their solubility in a hydrocarbon mixture was quite high. The high-molecular-weight portion of the tars, which did not distill in vacuum, did not dissolve in the hydrocarbon mixture.

Obviously, only the high-molecular part of the nonhydrocarbon compounds extracted from the fuels chromatographically should be classified among the tars that influence the operational characteristics of petroleum products.

This relationship was noted long ago by researchers. However, during the time when the chromatographic method of analysis, which enables us better to study the chemical structure of nonhydrocarbon impurities in petroleum products, was not being used, a classification of tars was developed on the basis of their solubility in certain chemical solvents. This method is extensively used at the present time.

One classification distinguishes

neutral tars, which are insoluble in alkalis and acids and quite

soluble in petroleum distillates;

asphaltenes, neutral substances that are not soluble in the light gasolines from which they separate, but are quite soluble in benzene, chloroform, and carbon disulfide.

carbenes, which are asphaltene condensation products that are not soluble in carbon tetrachloride, benzene, chloroform or carbon disulfide; they are to some extent soluble in pyridine.

carboids, substances formed from asphaltenes at elevated temperatures and insoluble in benzene and other solvents;

asphaltogenic acids, tars that are soluble in alkalis and solvents such as benzene.

It is perfectly obvious that the high-molecular part of the nonhydrocarbon impurities, which cannot remain in the form of a true solution in a hydrocarbon medium and precipitates out as a second phase as a result of oxidative and condensation transformations, should be included among the asphaltenes, carbenes, carboids and asphaltogenic acids. On the other hand, the soluble part represents a mixture of nonhydrocarbon compounds from which condensation products can be obtained. At the same time, they are of interest as a source for new chemical compounds that are not used at the present time.

It is interesting to compare the elementary compositions of the nonhydrocarbon impurities, their high-molecular parts, the solid deposits that form in the fuels at elevated temperature, the varnishes deposited on engine pistons, their scales and other transformation products (Table 40).

As would be expected, the elementary compositions of petroleum tars and the tars of its high-molecular part, which is insoluble in the hydrocarbon mixture (asphaltenes) differ little. Their compositions are characterized by extremely high contents of sulfur, nitro-

gen and oxygen. In essence, all other transformation products of the high-molecular part of the nonhydrocarbon impurities are characterized by the same property, irrespective of their phase composition. The data presented in the table leave no doubt that the sources of tar, sludge, scale-deposit, and varnish formation at both normal and elevated temperatures are the nonhydrocarbon impurities that are present and accumulate in the petroleum products. Their quantity, and, consequently, the quantity of the oxidative-condensation products will depend on the chemical composition of the petroleum products and the operational conditions, and temperature conditions in particular.

COMPOSITION AND CHARACTERISTICS OF SLUDGES

Ash-forming elements are detected in tars, sludges, deposits and varnishes. Their quantity increases considerably as a result of corrosion processes, which are intensified at elevated temperature. Numerous metals and nonmetals have been detected by spectral analysis among the ash-forming elements of tars and sediment. The quantities of iron, copper, zinc and silicon are particularly large. Table 41 lists ash compositions for deposits and sludges obtained on the filters of systems operating on type T fuels. The composition of the deposit and sludge ash shows elements that accumulate on refinement (Na, Mg, Ca), in the process of storing and transferring the fuel (Fe, Zn), during operation (Cu, Cd, Pb, Zn), due to contamination by atmospheric dust (Si, Al), etc. All of these ash-forming elements were present in the tars, deposits and sludges. This means that the mineral part, together with the organic nonhydrocarbon impurities, assumes an active importance in the formation of substances that precipitated from the petroleum products under certain conditions in the form of a second phase.

It follows from this that the "ash" elements of fuels have a no

TABLE 41

Content of Certain Elements in Sludge Ash and Sediment of Type T Fuels (in %)

| 1 Элементы | 2 Топливо-заправщик (25°) | 3 Самолет (45°) | Стенд (120° в топливе 0,045% меркаптановой серы) | 5 Стенд (150°) | 6 Латунный радиатор (135°) |
|---|---|---|---|---|---|
| Fe | 30 | 10 | 10 | 1—4 | 11 |
| Cu | 1,0 | 13 | 29 | 41,4 | 36,8 |
| Al | 0,3 | 1,0 | 0,4 | 3,0 | 0,4 |
| Ca | 0,3 | 1,0 | 0,1 | 0,3—1,0 | 3,0 |
| Mg | 0,2 | 1—2 | 0,4—1,0 | 1,0 | 1,0 |
| Sn | 0,3—1,0 | 10—15 | 1,0 | 0,3 | 0,04 |
| Cd | 1—3 | 10 | 1,0 | — | 1,0 |
| Si | 3—6 | 3—10 | 1—3 | 1,0 | 1,4 |
| Zn | 20—30 | 1—3 | 10—15 | 3,0 | 10 |
| Pb | 0,4—1,0 | 0,4—1,0 | 1,5 | 1,3 | 1—4 |
| Mn | 0,3 | 1,0 | 0,1—0,3 | 1—3 | 0,3—1,0 |
| Na | 0,4—1,0 | 11,0 | 1,0 | 5,0 | 1—3 |

1) Element; 2) fueling pump (25°); 3) aircraft ( °); 4) stand (120° in fuel with 0.045% of mercaptan sulfur); 5) stand (150°); 6) brass radiator (135°).

less detrimental influence on the operational properties of fuels and oils than the high-molecular part of the organic nonhydrocarbon impurities.

Depending on the chemical nature of the "ash" elements and the particle size of the solids that form in fuels and oils, there arises an additional danger of abrasive wear of components of mechanisms manufactured with high precision and small tolerances.

In diesel fuels and mazouts, the processes in which insoluble deposits form and accumulate develop with considerable speed, even at low temperatures. Growth of these particles, which have initial sizes ranging from 0.1 to 1 μ, takes place during storage and particularly during storage at high temperature. In diesel fuel, heating to 43° for 12 weeks was attended, apart from an increase in the absolute amount of insoluble residue, by an increase in the size of the largest particles from 2.8 to 10.4 μ [13].

It was estimated that 1 mm [sic] of mazout contained [14] 100 solid sediment particles from 20 to 30 μ in diameter, 2200 particles be-

tween 5 and 20 μ, and 98,000 particles from 1 to 5 μ.

The solid-particle content in standard TS-1 fuel was investigated under the supervision of I.N. Antipov-Karatayev at the Soil Institute imeni V.V. Dokuchayev, Academy of Sciences USSR.

Using the microscopic method of dispersion analysis, the content of solid particles prior to filtration was established at 0.056% by weight, while after filtration through a standard fuel-pistol filter it dropped to 0.024% by weight.

Table 42 shows the distribution of solid particles in the fuel by sizes.

TABLE 42

Distribution of Solid Particles in Fuel TS-1 by Sizes (in %)

| 1 Размер частиц, мк | 2 В исходном топливе | После фильтра топливозаправщика 3 |
|---|---|---|
| 4 | | |
| <5 (в среднем 2,48) | 52,50 | 64,40 |
| 5—10 (в среднем 6,41) | 24,50 | 18,10 |
| 10—50 (в среднем 14,70) | 22,66 | 17,35 |
| 50—80 (в среднем 61,20) | 0,15 | 0,07 |
| >80 | 0,07 | 0,09 |

1) Particle size, μ; 2) in initial fuel; 3) after passage through fuel-pistol filter; 4) averaging.

The deposit on the filter consisted of 5.98% of hygroscopic moisture, 68.59% of organic substances that could be removed on roasting, and 8.86% of ferric oxide.

The authors of the report conclude that the tarry substances in the fuel should be regarded as a peptizer for mechanical impurities.

With increasing temperature, the sediment-particle size in fuels and oils shows a disproportionate increase.

It is evident from the example furnished by fuels boiling in the ligroin-kerosene range that the sediment-particle size increases no-

TABLE 43

Variation of Sediment-Particle Size as a Function of Temperature to Which Fuel Is Heated [16]

| 1 Фильтры | 2 Топливо Т-5 (ГОСТ 9145-59) | | | | 3 Топливо Т-1 (ГОСТ 4138-49) | | | | 4 Топливо ТС-1 (ГОСТ 7149-54) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 5 температура нагрева топлива, °С | | | | | | | | | | | |
| | 120 | 150 | 200 | 250 | 120 | 150 | 200 | 250 | 120 | 150 | 200 | 250 |
| 6 Стеклянный № 4; задерживается осадка, *мг*/100 *мл* . . . . . | 1,9 | 4,9 | 0,6 | 0,4 | 5,2 | 7,5 | 2,0 | 1,7 | 3,4 | 6,9 | 1,3 | 1,0 |
| 7 Осадок на других фильтрах, % от задержанного на стеклянном № 4 | | | | | | | | | | | | |
| 8 Бумажный с отверстиями 6—7 *мк* . . . . | 81,5 | 94 | 100 | 100 | 70 | 97,5 | 100 | 100 | 61 | 97 | 100 | 100 |
| 9 Металлический с отверстиями, *мк*: | | | | | | | | | | | | |
| 15 | 26,4 | 61 | 100 | 100 | 24 | 74,6 | 100 | 100 | 24,6 | 63 | 100 | 100 |
| 30 | 5,2 | 33,4 | 100 | 100 | 2,3 | 47,1 | 100 | 100 | 2,9 | 47,7 | 100 | 100 |
| 50 | 0 | 26 | 54 | 63,4 | 0 | 30,7 | 47,5 | 53 | 0 | 34 | 44,4 | 60 |
| 120 | 0 | 4 | 38,5 | 44,4 | 0 | 13,6 | 15 | 18 | 0 | 8 | 15 | 30 |

1) Filter; 2) fuel T-5 (GOST 9145-59); 3) fuel T-1 (GOST 4138-49); 4) fuel TS-1 (GOST 7149-54); 5) heating temperature of fuel, °C; 6) glass No. 4; residue trapped in mg/100 ml; 7) deposit on other filters, % of that trapped on No. 4 glass filter; 8) paper with 6 — 7 μ holes; 9) metallic filter with hole sizes in μ.

ticeably with increasing temperature. An increasingly large quantity of sediment is trapped on filters with large openings (Table 43).

This is nicely illustrated by Fig. 76, which shows photographs made at a magnification of 80 of the sediment that formed in the fuel after 6 hours' heating in autoclaves at various temperatures in contact with bronze.

To minimize the influence of oxidative processes, the autoclaves were rinsed with nitrogen prior to the test, and the fuel was tested at an initial nitrogen excess pressure of 1 atmosphere.

Under these conditions, the oxidation processes were extremely

limited and could take place only at the expense of the residual oxygen in the liquid phase and oxygen impurities in the nitrogen (0.6 – 0.8%). The extremely small amount of sediment obtained fully confirmed the hypothesis set forth above; it was the more interesting to observe the change in particle size of these sediments as a function of temperature as a result of condensation processes.

The total weight of sediment formed reaches its maximum at a certain temperature and then drops regardless of further temperature increases. This effect finds its explanation when we consider the optimum conditions for oxidation of unstable components in a hydrocarbon mixture.

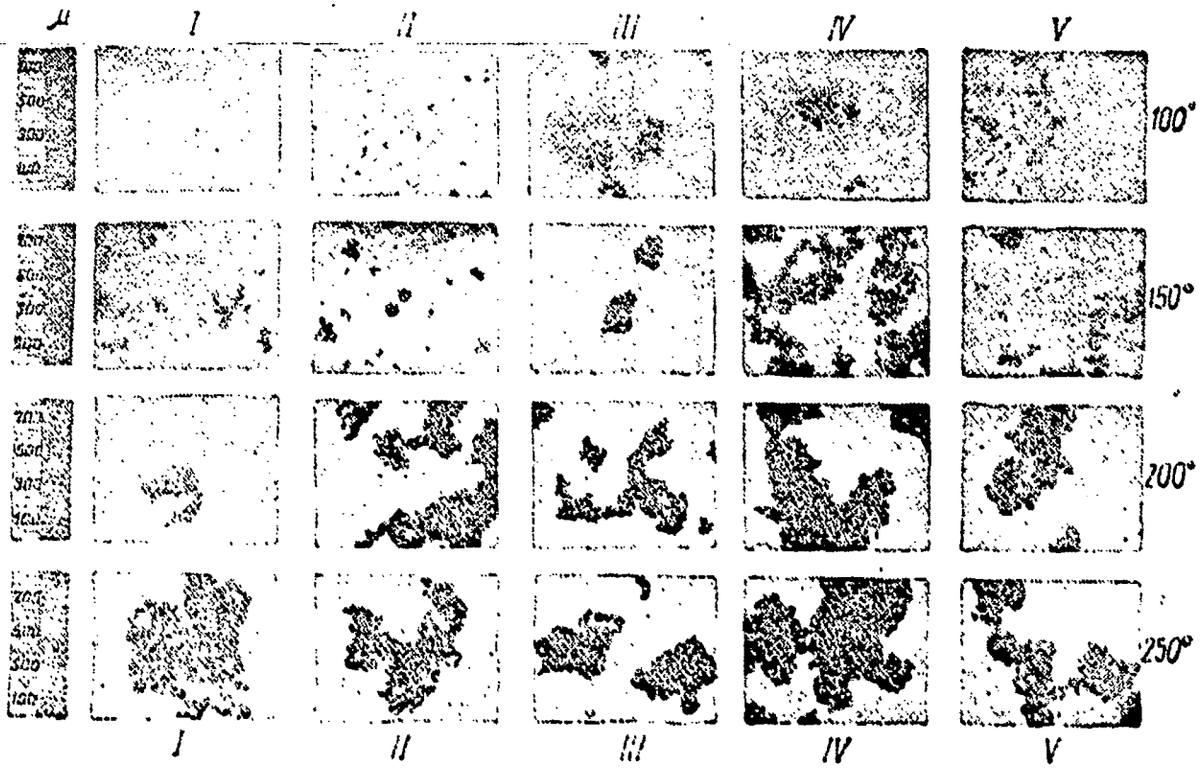


Fig. 76. Influence of temperature on condensation and particle-size increase in fuel sediment. I) T-5 fuel; 2) T-1; 3) TS-1; 4) T-2; 5) T-2 with cracking component.

As we indicated earlier, tar-, sediment- and varnish formation in fuels and oils take place as a result of oxidative condensation of non-hydrocarbon impurities. Oxidation of this type takes place in the liq-

uid phase, where the hydrocarbon mixture is, as it were, a medium in which new oxygen compounds form from the unstable hydrocarbons and the nonhydrocarbons present are subjected to further, more profound transformations. The higher the temperature, the more intensive is the development of the oxidation process. With increasing temperature, however, the vapor pressure of the hydrocarbons above the liquid phase will increase, with the result that diffusive penetration of atmospheric oxygen into the medium being oxidized is restricted. In other words, the exchange necessary for normal progress in liquid-phase oxidation is disturbed.

The oxidation will be least pronounced at the boiling point of the hydrocarbon mixture.

As we approach the boiling point, the oxidation process in the liquid phase dies out, culminating in condensation of the high-molecular oxidation products that have already formed. In the gaseous phase above the product, the concentration of oxygen by weight drops with increasing temperature and, consequently, with increasing quantities of hydrocarbon vapor. If, however, the oxygen concentration were adequate, development of oxidation processes in the gaseous phase would require incomparably higher temperatures (400 - 500°) than can be observed. Consequently, oxidation of the nonhydrocarbon compounds of fuels and oils will intensify only up to the temperature at which the petroleum-product vapor pressure increases sharply.

Each petroleum product will be characterized by its own equilibrium-boiling temperature, and by its own type of vapor-pressure variation on heating. Temperatures of maximum sediment formation can be established in accordance with this.

Table 44 shows the variation of the equilibrium-boiling temperatures as functions of the pressures developed on heating for fuels

that boil in the ligroin-kerosene fractions.

For such fuels, which have similar production methods and unstable-component contents, the maximum-sedimentation temperature lies in the range from 150 – 200° [17, 18].

As the heating temperature is further increased, the quantity of sediment formed diminishes and becomes very small at 250°. Consequently, the problem of sedimentation at heating temperatures above 200° is not pressing for direct-distilled ligroin-kerosene fractions unless the process takes place at an elevated air temperature.

This applies only for cases in which the heating rate is so high that precipitation of a solid phase does not occur on passage through the maximum-sedimentation temperature range. We note that in modern type T fuels, sedimentation is observed 3 – 4 hours after a temperature of 150° has been reached. Naturally, this limit will move into a higher-temperature region for higher-boiling fuels, and the more so for oils. The above does not apply to the corrosive aggressiveness of petroleum products. In the presence of corrosively active components that are stable under these conditions, the corrosion aggressiveness of fuels and oils increases with temperature.

TABLE 44

Variation of Equilibrium-Boiling Temperature of Fuels as a Function of Pressure Developed on Heating

| 1 Топливо | Нормальное давление | | 5 Повышенное давление | | | |
|---|---|---|---|---|---|---|
| | 3 пределы выкипания, °С | 4 температура равновесного кипения | 6 температура нагрева, °С | 7 давление над топливом, ат | 3 пределы выкипания, °С | 4 температура равновесного кипения, °С |
| Т-2 | 62—237 | 116,6 | 120<br>150<br>200<br>250 | 2,20<br>2,65<br>4,85<br>8,00 | 85—290<br>105—310<br>130—345<br>154—380 | 147<br>160<br>190<br>214 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 ТС-1 | 137—226 | 164,6 | 120<br>150<br>200<br>250 | 1,55<br>1,90<br>2,70<br>4,05 | 155—243<br>164—256<br>176—270<br>205—305 | 183<br>190<br>205<br>236 |
| Т-1 | 143—267 | 178,8 | 120<br>150<br>200<br>250 | 1,45<br>1,85<br>2,35<br>4,30 | 157—284<br>170—296<br>185—315<br>205—345 | 188<br>202<br>208<br>242 |
| Т-5 | 188—308 | 233,9 | 120<br>150<br>200<br>250 | 1,25<br>1,40<br>1,80<br>2,65 | 195—316<br>200—320<br>210—336<br>230—360 | 245<br>250<br>258<br>280 |

1) Fuel; 2) normal pressure; 3) boiling range, °C; 4) equilibrium-boiling temperature; 5) elevated pressure; 6) heating temperature, °C; 7) pressure above fuel, atmospheres; 8) TS-1.

## CONCERNING THE MECHANISM OF FORMATION OF A SOLID PHASE IN A HYDROCARBON MEDIUM

We have yet to consider the mechanism of formation of the solid phase that precipitates out of a hydrocarbon mixture in the form of viscous tars, solid deposits, sediment, varnishes and other condention products as a function of temperature and other conditions.

The initial fuels or oils, which are free of mechanical impurities, may be regarded as true solutions of nonhydrocarbon organic compounds in a hydrocarbon medium. The correctness of this conception is confirmed by the fact that thoroughly filtered type T fuels give a clear background under an electron microscope at a magnification of 10,000. Molecules that are, as it were, overloaded by heteroatoms form in an early stage of the oxidative transformations of the hydrocarbons and nonhydrocarbon impurities, and some of these form the material for formation of a solid phase. Their presence in the hydrocarbon mixture changes the physical nature of the solution. Such a solution may be regarded as a semicolloidal system in the sense that it simultaneously contains a considerable quantity of a truly soluble part of the mate-

rial from which a colloidal phase forms in the surrounding disperse medium [19]. On the whole, such systems, which are characterized by particles much smaller than 1 μ in diameter, are classified as colloids with maximum dispersion and stability.

Let us recall that the dispersion of such systems is determined by the molecular nature of the two phases and their state.

Further transformations take place with changes in phase composition under the influence of various factors, primarily temperature. Instability of state intervenes at this point; we observe enlargement and condensation of solid-phase particles, which precipitate from the system in the form of viscous tars or a deposit. The nature of the solid phase that separates out is determined primarily by temperature conditions. At low temperatures, it takes the form of viscous tars. The process in which they form requires months and years. At higher temperatures, flocculent solid particles will form. The rate of their formation will be reckoned in hours. A varnish film will form at a hot surface at temperatures of 250° and higher. The higher the temperature of the medium, the richer in carbon will be the molecule of the solid phase, since it has been subjected to profound thermal destruction. The final products of this destruction are sootlike formations which, of course, are far from being pure carbon but are extremely rich in it due to processes of thermal decomposition of the high-molecular-weight part of the nonhydrocarbon impurities in the fuels or oils.

Contamination by "ash" elements contributes very greatly to breakdown of the colloidal system with formation of a precipitating second phase. Extremely fine particles of metal-corrosion products and atmospheric dust which penetrate into the fuels or oils act, as it were, as centers around which the organic particles of high-molecular-weight, nonhydrocarbon impurities aggregate. This is why large quantities of

ash elements are detected in the deposits, varnishes and sediments irrespective of the source from which they have accumulated. Their elimination from the petroleum products would result in considerable restriction of the tar- and sludge-formation processes.

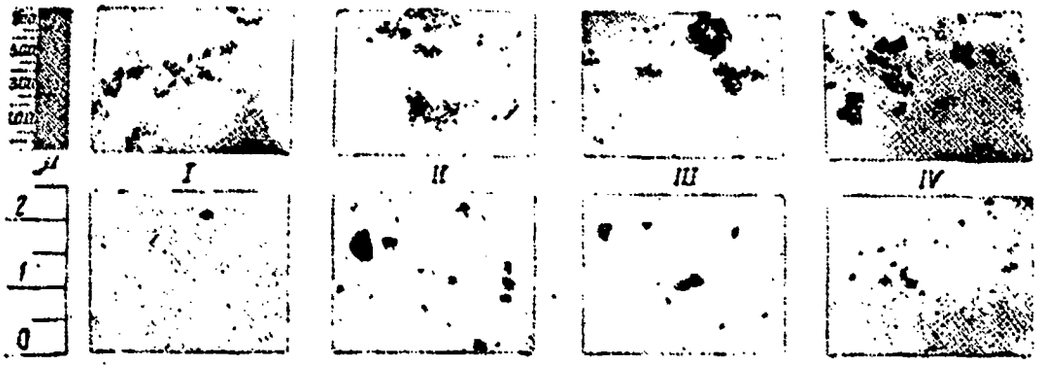


Fig. 77. Insoluble deposits in fuels subjected to heating in autoclaves at 150°. I) T-5; II) T-1; III) TS-1; IV) T-2.

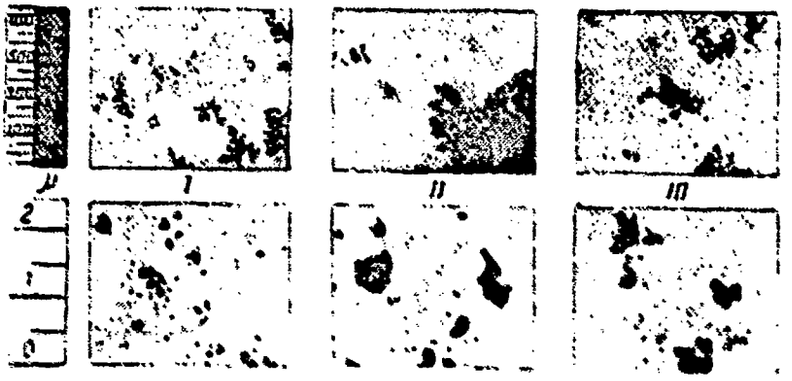


Fig. 78. Insoluble deposits in fuels subjected to heating at 150° in a system communicating with the atmosphere. I) T-5; II) T-1; III) TS-1.

It has been noted that the oxidation products of hydrocarbons and the nonhydrocarbon impurities, which are characterized by aliphatic structure, are held in the form of true solutions with the hydrocarbons considerably longer than systems with cyclic (preferentially aromatic) structure.

It has been established that aromatic structures form the basic mass of the tars. This is what determines the nature of the colloidal

systems. They are lyophilic toward aromatic hydrocarbons and lyophobic toward hydrocarbons with the aliphatic structure.

Fig. 79. T-2 fuel after heating at 120° in a system communicating with the atmosphere.

Obviously, the dispersion of the colloidal system, its physical state, and the rate at which it breaks down to liberate a solid phase depend to a considerable degree on the chemical composition of the petroleum products.

All this is clearly evident on microphotographs of direct-distilled fuels that boil in the range of the ligroin-kerosene fractions. Figures 77 and 78 show fuels after 6 hours of heating in contact with bronze at a temperature of 150°, while Fig. 79 shows them after heating at 120°.

The upper row shows microphotographs of fuels made immediately after the test at a magnification of 80. Particles of deposits that represent an aggregated system of varying density are seen clearly here.

The lower row shows electron microphotographs of fuels that had been subjected to preliminary filtration through a dense filter after the test. No solid particles could be seen in these filtrates at a magnification of 600. At a magnification of 10,000, however, a large number of solid particles smaller than 1 μ in size is detected in them. It is perfectly obvious that here we had a colloidal system whose breakdown, together with aggregation of a solid phase, resulted in deposits that precipitated from the hydrocarbon mixture.

Figure 79 shows that there is apparently no solid phase in fuel T-2 after testing at 120° and at a magnification of 80. However, a photograph taken with an electron microscope (lower frame) shows that

heating of the initial fuel, which was a true solution, turned it into a colloidal system with particles ranging from 0.1 to 0.4 μ in size.

The rate and profundity with which the colloidal-system solid phase aggregates is strongly influenced by the elevation of temperature to which the system is subjected and the dirt particles, which are capable of acting as coagulation centers for the solid phase.

Thus, two processes share the basic role in formation of tars, deposits and sludges in petroleum products: 1) oxidation of unstable hydrocarbons and nonhydrocarbon impurities to varying depths; 2) condensation of the oxidation products to form a precipitating second phase.

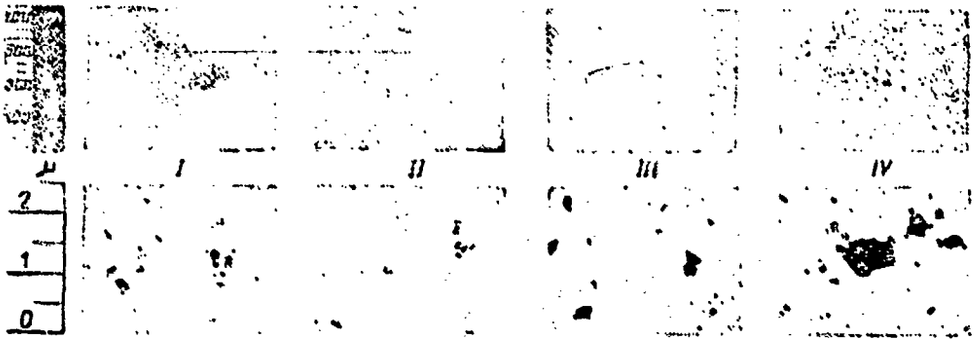


Fig. 80. Fuel with surface-active additive after 6 hours of heating in contact with bronze at 150°. I) T-1; II) TS-1; III) T-5; IV) T-2.

These undesirable processes can be prevented by purification and fine filtration of petroleum products. The use of additives may also be found highly effective (see Chapter 17); these should combine two functions – those of antioxidants and dispersing agents.

Antioxidant additives make it possible to inhibit or prevent oxidation processes in fuels and oils, particularly in the stage in which high-molecular-weight compounds form.

Dispersing, or, as they are sometimes called, detergent additives enable us to prevent breakdown of the colloidal system in cases where such a system has formed and aggregation of the solid phase into pre-

cipitating tars, deposits and sludges.

As a result of adsorption or chemosorption, a minute particle of the colloidal system is "protected" by a monomolecular layer of additive, with the result that breakdown of the colloidal system and, consequently, coagulation and subsequent precipitation of a solid phase are prevented. Together with this, the negative influence of the non-hydrocarbon impurities present and the processes of their oxidative condensation in the petroleum products are localized to varying degrees.

The results obtained with an effective surface-active dispersing additive may be seen in Fig. 80.

After prolonged heating at 150°, no particles of a solid coagulated phase are seen in fuels containing such an additive when inspected at a magnification of 80. The fuel is transparent (see top row of photographs). Only at a magnification of 10,000 under an electron microscope do we see solid-phase particles with sizes from 0.2 to 0.5 μ (see lower row of photographs). In other words, we were dealing in this case with a stabilized colloidal system.

When such additives are employed, commercial fuels and oils may, in the majority of cases, be employed in thermally stressed systems without any further technological processing (see Chapter 23).

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## Chapter 11

## BEHAVIOR OF FUELS AT LOW TEMPERATURES

When we speak of low-temperature properties of fuels we refer to those specific features encountered in the behavior of fuels as their temperatures are reduced, and as a result of which it becomes difficult to provide for the normal flow of fuel through the fuel-feed system of an engine; in addition, there may be difficulties in the flow of fuel during transportation, pumping, delivery, and fuel servicing, in addition to the difficulties that may be encountered in the starting of a cold engine.

The most important changes in fuel properties, taking place with a drop in temperature and impairing the operational characteristics of the fuel, involve the separation of a second liquid or solid phase from the fuel, causing the fuel to lose its mobility and producing a pronounced reduction in the pressure of the saturated fuel vapors. Moreover, with a drop in temperature the water vapors from the intake air condense in carburetor engines, resulting in ice formation on the throttle valves and on the walls of the carburetor.

During the fueling of the engine, with a fuel containing a solid phase in the form of crystals, the filters become choked with crystals as a result of which there is a pronounced drop in the capacity (output) of the fueling unit. With fuel feed from a tank through a fuel-feed system, the supply of fuel is at first disrupted and then completely stopped as a result of the choking of the filters with crystals.

As the fuel becomes immobile, it becomes difficult or completely

impossible to transfer it from the railroad tank cars, and this applies equally to the pumping of such a fuel or its utilization for servicing.

With a drop in the pressure of the saturated fuel vapors the volatility of the fuel diminishes and as a result it becomes difficult to start the engine. The increased deposition within the engine and the impairment of the quality of the lubricant employed are associated with this incomplete vaporization of the fuel at low temperatures.

As a result of carburetor icing, the amount of air that passes through the valves is restricted and the rpm of the engine is reduced — the engine begins to function intermittently. Under particularly unfavorable conditions, the icing of the throttle valve is so pronounced that it freezes completely shut and the engine ceases to function.

High-melting hydrocarbons, primarily of the paraffinic series in the fuel composition, and the water dissolved in the fuel or condensed from the air on the surface of the cold fuel are the factors responsible for the separation of the solid phase from the fuel. The loss of fuel mobility takes place either as a result of a pronounced increase in fuel viscosity (to hundreds and thousands of stokes), or as a result of the formation of a crystal lattice of high-melting hydrocarbons, and here the viscosity of the fuel is not yet of a magnitude adequate to preclude fuel mobility. It is for this reason that in the last case under dynamic conditions, i.e., in the case of the pumping of the fuel, the fuel-pumpability temperature may be 15-20° lower than the freezing temperature (point).

In an examination of the low-temperature properties of a fuel, we should dwell in some detail on the following problems.

1. The separation of high-melting hydrocarbons from the fuels at low temperatures.

2. The nature of the change in fuel viscosity with a reduction of

the fuel temperature.

3. The behavior of the water in the fuel and the water vapors in the intake system of the engine.

4. The volatility of the fuel at low temperatures.

## THE SEPARATION OF HIGH-MELTING HYDROCARBONS FROM FUELS AT LOW TEMPERATURES

The separation of high-melting hydrocarbons from fuels at low temperatures, with the subsequent formation of a crystalline structure, is the basic factor responsible for making the normal application of the fuels difficult. Not all hydrocarbons making up a fuel exhibit high melting points. As a rule, the greater part of the hydrocarbons in the composition of a fuel, and frequently the predominant mass of the hydrocarbons, exhibit low melting points.

The presence of a relatively small quantity of high-melting hydrocarbons (10-20%) in a fuel is completely sufficient to raise substantially the temperature for the initiation of crystallization and the solidification of fuels.

Of all the hydrocarbons in the paraffinic series which can be found in the composition of aviation gasolines, the highest melting point is exhibited by normal-structure hydrocarbons, if we exclude the overly branched symmetric-structure hydrocarbons. Since in contemporary aviation gasolines the presence of hydrocarbons with more than 7 to 8 carbon atoms as well as symmetric-structure hydrocarbons is virtually excluded, the paraffinic portion of the aviation gasolines is made up of hydrocarbons having a melting point below $-60^{\circ}$.

Naphthenic hydrocarbons which can be included in the composition of aviation gasolines, with the exception of cyclonexane and several other hydrocarbons having a melting point ranging from $-20$ to $-50^{\circ}$, also melt below $-60^{\circ}$. Because the content of cyclohexane as well as of

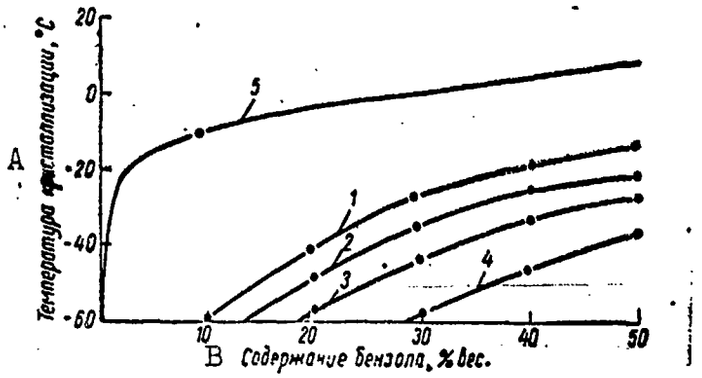


Fig. 81. The crystallization temperature of benzene as a function of the hydrocarbon composition of gasoline. 1) Alkylate; 2) B-70 gasoline; 3) 80% B-70 gasoline + 20% toluene; 4) toluene; 5) diesel fuel with a cetane additive; A) Crystallization temperature, °C; B) benzene content, % by weight.

other naphthenic hydrocarbons having a melting point above -50 to -60° is comparatively low in aviation gasolines, the naphthenic portion of the aviation gasolines is virtually also composed of hydrocarbons having a melting point below -60°.

With respect to aromatic hydrocarbons, some of these, having a high melting point, are either contained in noticeable quantities in base gasolines obtained by catalytic processes (xylenes), or are added to the base gasolines in the form of components to improve the antiknock properties of the fuels (pyrobenzene, benzene). Therefore the impairment of the low-temperature properties of aviation gasolines can be brought about solely through the presence of aromatic hydrocarbons, particularly benzene. The temperature at which the benzene is crystallized from the gasoline depends on the benzene content and its solubility in gasoline, this determined by the hydrocarbon composition of the latter (the gasoline). As can be seen from Fig. 81 the greater solubility is exhibited by the benzene in aromatic hydrocarbons, i.e., in the

hydrocarbons that are analogous to the benzene in structure, and the lowest solubility is exhibited by the benzene in the paraffinic hydrocarbons.

In automotive gasolines the content of aromatic hydrocarbons and particularly of benzene is not too great; the end-of-boiling for gasolines reaches 205°. Therefore, with the introduction into these automotive gasolines of a substantial quantity (more than 50%) of direct-distillation gasolines derived from paraffinic petroleums, the crystallization temperature for the automotive gasolines will be determined by the paraffinic hydrocarbons of normal structure. However, the highest-melting paraffinic hydrocarbon which can be found in the composition of a gasoline – undecane – exhibits a melting point of –25.6°; therefore, automotive gasolines, as a rule, have low crystallization temperatures.

A more urgent problem is the one having to do with the crystallization temperature for higher-boiling fuels – jet and diesel fuels. Unlike the aviation gasolines, the crystallization of these fuels is caused primarily by paraffinic hydrocarbons. This can be explained primarily by the fact that beginning with 180-210°, with the exception of certain mono- and bicyclic aromatic hydrocarbons of symmetric structure and, as a rule, not detected in the composition of petroleums, the highest melting points are exhibited by normal or slightly branched paraffinic hydrocarbons whose content in fuels derived from petroleums of a paraffinic base amount to 50-60%.

Moreover, as can be seen from Fig. 81, with the addition of paraffinic hydrocarbons the first portions (up to 2%) produce the sharpest increase in the crystallization temperature, and with a relatively small content of paraffinic hydrocarbons in the fuel, the pour point of the fuel increases markedly.

A pronounced increase in the solidification temperature of the

fuel, through the addition of insignificant quantities of high-melting normal paraffinic hydrocarbons, can be explained by their limited solubility in the hydrocarbons of other classes at low temperatures. With an increase in the fuel temperature, the solubility of the paraffinic hydrocarbons increases at first slowly and then sharply as the temperature of the medium approaches the melting point. The solubility of the paraffinic hydrocarbons is a function also of the melting point of the hydrocarbons and the nature of the solvent. With an increase in the melting point, the solubility of the paraffinic hydrocarbons in the fuel diminishes. The closer in structure the hydrocarbons making up the fuel to the paraffinic hydrocarbons, the better their solubility in the fuel. In addition to the purely paraffinic hydrocarbons, the crystallization of higher-boiling fractions of jet and particularly of diesel fuels is brought about also by monocyclic naphthenic and aromatic hydrocarbons that have long side chains of normal structure.

In jet and diesel fuels derived from petroleums having a naphthenic-aromatic base bicyclic naphthenic and aromatic hydrocarbons are predominant. It is for this reason that these fuels have, as a rule, rather low solidification temperatures (about $-40^{\circ}$ and lower).

Consequently, the tendency of aviation gasolines to crystallize is not a function of their chemical nature and is governed only by the presence of certain aromatic hydrocarbons in the gasolines, primarily by the presence of benzene, and with a limited benzene content no crystallization of aviation gasolines can be detected during their utilization. The same can be said of automotive gasolines.

Fo jet and diesel fuels the tendency to crystallization is determined primarily by their chemical composition.

In the cooling of the fuel (to temperatures corresponding to the total solution of the paraffinic hydrocarbons contained within the

composition of the fuel) the highest-melting paraffins begin to settle out and the fuel becomes turbid. This temperature has been designated as the temperature for the initiation of fuel crystallization or, as was the practice earlier, the cloud point.

Normal paraffinic hydrocarbons both in the pure state as well as in the dissolved state in the fuel are capable of supercooling in the absence of crystallization centers or seeds. As a result, they settle out from the fuel and crystallize at a lower temperature than their solubility temperature for the given concentration in the fuel. The supercooling ratio is a function of the nature of the fuel and amounts, for example, for a 10% solution of cetane to 8-21° [3]. In commercial fuel samples, pronounced supercooling is not observed. This can be explained by the fact that the tiniest of mechanical-admixture particles are always present in fuels and as a result it becomes possible to produce air bubbles which serve as crystallization centers.

The shape and dimensions of the paraffinic crystals which settle out from the fuel are functions of the nature of the fuel, the concentration of the paraffinic hydrocarbons, the cooling rate, and the presence of surface-active agents in the fuel. It should be pointed out that there is no common opinion with respect to the shape of the paraffinic crystals. Some researchers note that with the cooling of particularly concentrated solutions of paraffinic hydrocarbons acicular crystals are formed, and the paraffinic hydrocarbons crystallize in the form of plates out of weak and medium-concentration solutions [4, 5]. Other researchers maintain that the crystal shape is a function of the structure of the paraffinic hydrocarbons - normal paraffinic hydrocarbons crystallize into a plate-like shape, whereas the isoparaffins crystallize into an acicular shape [6-8].

A.S. Irisov and V.N. Lapikura [3] showed by means of microphoto-

graphy (including motion pictures) of the crystallization process in cetane that the shape of the cetane crystals is determined by the nature of the solvent. Plate-like crystals are separated out of solvents that are paraffinic in nature. Fiber-like crystals are precipitated from naphthenic solvents. In individual cases, during crystallization from a supercooled solution and in the absence of seeds, the formation of spherulites was observed.

Grain-like (globular) shaped crystals are precipitated from solutions of bicyclic aromatic hydrocarbons with short side chains. Mixed crystals – plates and grains – are first formed out of solutions of monocyclic aromatic hydrocarbons having long side chains; subsequently, the grain-shaped crystals proved to be less stable, whereas the plate crystals grow together to form a strong grid.

Some investigators have pointed out that neither the solvent nor the quantity in which it is employed have any effect on the shape of the crystals [9, 10].

The nature of the medium has an effect on the dimensions of the crystals as well as on the rate of their growth. D.L. Gol'dshteyn, Z.V. Veksler, and G.Ye. Zhuravlev [11] demonstrated that paraffin crystals separated from a fuel are substantially larger than the same crystals within the fuel; the length of the paraffin crystals in synthol is 3-4 μ, and in a fuel derived from Surakhany petroleum this crystal is 9-12 μ long; in a fuel derived from Groznyy paraffinic petroleum the crystal is 20-30 μ long. With a reduction in the concentration of high-melting hydrocarbon in the fuel, the dimensions of the crystals increase. For a 10% solution of cetane, the dimensions of the crystals attain 10 μ; for a 5% solution, 30 μ; and for a 2% solution, 35 μ and more [3]. The crystallization of paraffin from high-solidification diesel fuels begins at many centers with the formation of acicular crystals having an average

dimension of about 5 μ and these grow comparatively fast, forming a characteristic grid with needles 10-16 μ long. The crystallization of the paraffins in low-solidification fuels is different in character – the crystals are formed from a few centers, they grow substantially more slowly, attaining lengths of 16-25 μ, and they yield a grid that is not quite as dense. Moreover, the precipitation of paraffin crystals begins at a temperature that is some 5-10° higher than the solidification temperature of the fuel [3].

When surface-active agents are present during the crystallization of fuels, small paraffin crystals are formed. If the fuel containing the paraffin crystals is kept at a constant temperature the crystals are reinforced as a result of which the number of larger crystals increases and the dispersion of the system is reduced.

When a fuel is cooled to a temperature that corresponds to the beginning of the crystallization of the paraffins contained within the fuel, only an insignificant portion of the paraffinic hydrocarbons dissolved within the fuel are separated from it. With subsequent reduction in temperature, the quantity of precipitated paraffin crystals from the fuel increases. The precipitated crystals grow together, forming reticular and cellular structures which include the uncrystallized component parts of the fuel within the cells. As a result, the fuel loses mobility and solidifies.

The difference between the temperatures of the beginning of crystallization and the temperatures of a fuel solidification is not constant and is a function of the quantity of paraffinic hydrocarbons contained within the fuel, as well as being a function of the melting point of these paraffinic hydrocarbons, the presence of surface-active agents in the fuel, and also to some extent a function of the fuel viscosity. As can be seen from the data presented in Table 45, the greatest differ-

ence, as high as 28-35°, is exhibited by diesel fuels derived from petroleums of a naphthenic or naphthenic-aromatic base (Koschagil', Neftedag), containing small quantities of paraffinic hydrocarbons.

TABLE 45

The Temperature of the Beginning of Crystallization and the Solidification Temperature for Various Diesel Fuels

(D.L. Gol'dshteyn, Z.V. Veksler)

| 1 Топливо | 2 Температура, °С: 3 начала кристаллизации | 4 застывания |
|---|---|---|
| 5 Дизельное топливо из косчагыльской нефти | −26 | −54 |
| 6 Дизельное топливо из нефтедагской нефти | −14 | −49 |
| 7 Керосин из сураханской нефти | −39 | −56 |
| 8 Дизельное топливо из сураханской нефти | + 4 | − 7 |
| 9 Керосин из ишимбайской нефти | −10 | −30 |
| 10 Дизельное топливо из ишимбайской нефти | 0 | − 5 |
| 11 Керосин из грозненской нефти | −17 | −20 |
| 12 Дизельное топливо из грозненской нефти | − 2 | − 6 |

1) Fuel; 2) temperature, °C; 3) beginning of crystallization; 4) solidification; 5) diesel fuel from Koschagil' petroleum; 6) diesel fuel from Neftedag petroleum; 7) kerosene from Surakhany petroleum; 8) diesel fuel from Surakhany petroleum; 9) kerosene from Ishimbay petroleum; 10) diesel fuel from Ishimbay petroleum; 11) kerosene from Groznyy petroleum; 12) diesel fuel from Groznyy petroleum.

With an increase in the content of paraffinic hydrocarbons within the fuel, there is a drop in the difference between the temperature marking the beginning of crystallization and the temperature of solidification. For Surakhany kerosene containing 35% paraffinic hydrocarbons this difference amounts to 17°, whereas for Groznyy kerosene in which the content of paraffinic hydrocarbons reaches as high as 60%, the difference amounts only to 3°. There is a substantial reduction in the discontinuity between the temperature marking the beginning of crystallization and the solidification temperature as the melting point of the paraffinic hydrocarbons in the fuel rises. Therefore, despite the fact

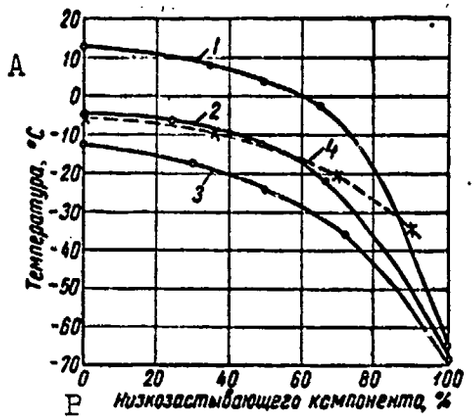


Fig. 82. Influence of low-solidification component on cloud point and temperature of solidification of a high-solidification component. 1) Solidification temperature of a mixture of Groznyy solar distillate + Binagadi gas oil; 2) the same for a mixture of Groznyy gas oil + Balakhany gas oil; 3) for a mixture of Surakhany gas oil + Bibieybat kerosene; 4) the cloud point for a mixture of Surakhany gas oil and Binagadi kerosene; A) Temperature, °C; B) low-solidification component, %.

that diesel fuels derived from Surakhany, Ishimbay, and Groznyy petroleums contain fewer paraffinic hydrocarbons than kerosenes derived from the same petroleums because of the higher melting point of the paraffinic hydrocarbons contained in diesel fuels, the discontinuity (difference) betweeen the temperature marking the beginning of crystallization and the solidification temperature for diesel fuels is less than in the case of kerosenes.

Surface-active agents, increasing the degree of dispersion in the system, increase the discontinuity (difference) between the temperature marking the beginning of crystallization and the solidification temperature of the fuel. If the paraffins are precipitated in an extremely viscous medium, the difference between the temperature of the beginning of crystallization and the solidification temperature is not very great.

Low-temperature properties of fuels containing high-melting hydrocarbons, primarily paraffins, can be improved either by the removal of these hydrocarbons by some method (deparaffinization) or by the conversion of these hydrocarbons into hydrocarbons of other classes (thermal or catalytic refining), or by the mixing of such fuels with low-solidification fuels; another possibility is the addition of appropriate additives to these fuels – depressors (see Chapter 14).

Deparaffinization and thermal or catalytic refining of fuels makes

it possible substantially to reduce the temperature marking the beginning of crystallization or solidification. However, in addition the cetane numbers of the fuel are reduced, as is the yield of the final product. Moreover, the execution of these processes from a production standpoint is cumbersome. Therefore the above-enumerated methods have to the present time not gained widespread acceptance. The removal of the paraffins by means of urea should be regarded as promising.

As can be seen from Fig. 82 there is no additive change in the temperatures marking the beginning of crystallization and solidification when high-solidification fuels are mixed with low-solidification fuels, but rather there is observed a shift in these temperatures in the direction of the high-solidification component. Therefore in order to achieve a sufficiently pronounced reduction in the temperatures of the beginning of crystallization and fuel solidification it is necessary to add a somewhat larger quantity of low-solidification fuel (up to 70-80% and more) which from a practical standpoint makes no sense at all.

## THE NATURE OF THE CHANGE IN FUEL VISCOSITY WITH A REDUCTION IN FUEL TEMPERATURES

Fuel viscosity is an extremely important operational characteristic of quality and this applies primarily to diesel fuels as well as to jet fuels. Viscosity determines fluidity and ease of fuel supply to the spray nozzles. In combination with the density and surface tension of the fuel, viscosity has a substantial effect on the degree of fuel atomization and the range of the stream. Given low fuel viscosity, atomization is better but the range of the stream is diminished. With reduced viscosity there is an increase in the amount of fuel that is drawn in through leaks in the pump. As the fuel viscosity increases, the depth (range) to which the stream can penetrate increases. But beyond a cer-

tain viscosity limit, the degree of atomization is markedly reduced and the drop dimensions increase, as a result of which the vaporization conditions are impaired and complete combustion of the fuel is not attained; in addition, the fuel flow rate and the amount of exhaust smoke are increased. The effect that the viscosity of a diesel fuel [12] exerts on the functioning of an engine is presented below.

| 1 Вязкость, $\eta_{50}$, *сст* | 7 | 9 | 15 | 16 | 40 | 49 | 65 |
|---|---|---|---|---|---|---|---|
| 2 Удельный расход, *г/л. с. ч.* | 246 | 250 | 247 | 250 | 260 | 315 | 328 |
| 3 Дымность, усл. ед. | 77 | 76 | 82 | — | 85,6 | 96 | 95,8 |

1) Viscosity, $\eta_{50}$, centistokes; 2) specific fuel consumption, g/hp·hr; 3) smoke content, conventional units.

An extremely viscous fuel offers great resistance in its passage through the fuel-feed system, and this results in the detachment of the fuel stream which, in turn, produces disruptions in the fuel feed to the pump. The maximum viscosity of a fuel at which the fuel supply ceases to provide for nominal (rated) engine power is referred to as limit [maximum] viscosity.

Depending on the design of the fuel-feed system of the engine, the value of the limit viscosity may change within a wide range. For example, for three various fuel-feed aircraft systems, the limit fuel viscosities amounted to 85, 160, and 210 centistokes, respectively, whereas for the fuel-feed system of the C-65 tractor the maximum fuel viscosity amounted to 2990 centistokes [11].

If the fuel is supplied under excess pressure, even if the latter is not too great, the limit viscosity of the fuel increases markedly. Therefore, the most vulnerable point in the fuel-feed system, limiting

the fuel supply, is that section from the tank to the pump in which the fuel is generally carried by gravity or under the action of a pump.

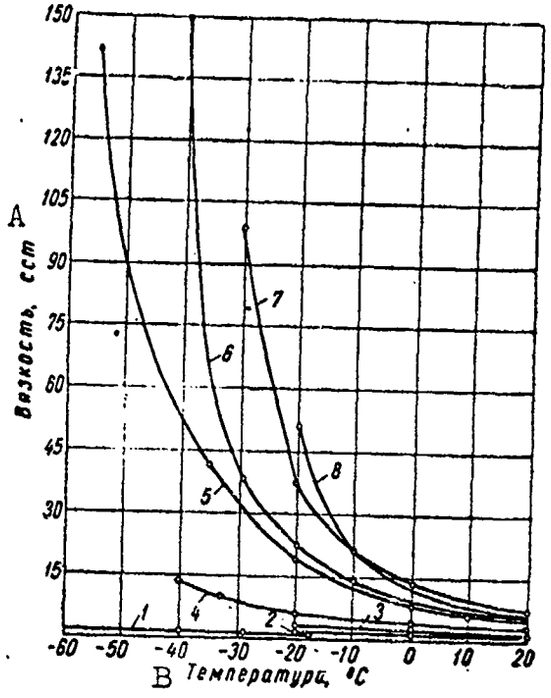


Fig. 83. Viscosity-temperature properties of various fuels. 1) n-Heptane; 2) aviation gasoline; 3) ligroin; 4) paraffin-base kerosene; 5) naphthenic-aromatic-base kerosene; 6) catalytic gas oil; 7) winter diesel fuel; 8) summer diesel fuel; A) Viscosity, centistokes; B) temperature, °C.

The normal atomization of a fuel in a jet engine is generally carried out when the viscosity of the fuel at $-50^{\circ}$ does not exceed 25 centistokes [16]. In diesel engines, at higher atomization pressures, the normal atomization of the fuel is achieved at a viscosity value in excess of 100-150 centistokes at $-40^{\circ}$.

The viscosity of the fuels used in carburetor engines has an effect on the quantity of fuel that passes through the nozzle. With a drop in viscosity the volume of fuel passing through the nozzle increases.

Figure 83 shows the viscosity-temperature curves for fuels used in various types of engines. As can be seen from the curves, the fuels differ substantially between one another both in terms of absolute viscosity as well as in terms of the nature of the change that the fuels undergo with a drop in temperature. In addition to the fractional composition, the chemical composition of the fuel also affects the nature (shape) of the viscosity-temperature curve; the heavier the fractional composition of the fuel, the more pronounced the effect of the chemical

composition of the fuel.

For example, for aviation and automotive gasolines below $-60^{\circ}$ the chemical composition has virtually no effect on the nature (shape) of the viscosity-temperature curve. For jet fuels of the kerosene type the effect of the chemical composition becomes noticeable, and in the case of diesel fuels the chemical composition determines the nature (shape) of the viscosity-temperature curve. The smoothest (flattest) viscosity curve is exhibited by paraffinic hydrocarbons, and the steepest curve is exhibited by aromatic hydrocarbons, particularly by bicyclic hydrocarbons.

It is natural that the utilization, at low temperatures, of fuels whose viscosity undergoes marked change with a drop in temperature involves considerable difficulties and not every fuel which exhibits good viscosity at positive temperatures will provide for engine operation at low temperatures. For example, a naphthenic-aromatic type of fuel cannot function in any one of the above-mentioned three systems reliably at temperatures below $40\text{-}45^{\circ}$.

For diesel fuels, and to a lesser extent for jet fuels, under certain conditions the appearance of a pronounced viscosity anomaly is characteristic, i.e., the so-called structural viscosity – the fuel is converted to the colloidal state, acquires plasticity, and a static limit shear stress appears within the fuel. As can be seen from Fig. 84, at $-10^{\circ}$ neither of the two fuels exhibits plasticity and flow can take place, given a small pressure head. At $-30^{\circ}$ plasticity appears in both of the fuels, and they acquire fluidity (flow sets in) with a pressure head of $\sim 0.1$ g/cm$^2$. At $-50^{\circ}$ fuel No. 2 becomes fluid only with a pressure head of 0.42, and fuel No. 1 requires a pressure head of 0.68 g/cm$^2$.

The supply of the fuel which exhibits this anomalous viscosity

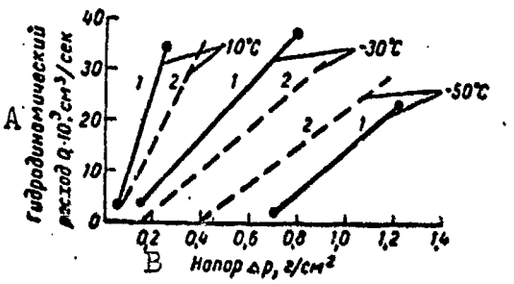


Fig. 84. Hydrodynamic flow rate of diesel fuel as a function of pressure head at low temperatures [14]. 1) Fuel No. 1; 2) fuel No. 2; A) Hydrodynamic flow rate $Q \cdot 10^3$, $cm^3/sec$; B) pressure head, $\Delta p$, $g/cm^2$.

from a tank to the pump is made difficult and cut short as a result of which the power of the engine diminishes.

The fuel-viscosity anomaly, i.e., the appearance of structures within the fuels, can be explained by the crystallization of paraffin and the consolidation of the paraffin into a structural grid. The temperature at which this structure is formed is a function of the concentration of paraffinic hydrocarbons in the fuel as well as a function of the melting point of these paraffinic hydrocarbons. With a large content of paraffinic hydrocarbons, particularly of high-melting hydrocarbons, the formation of a structure is observed within 1-2° prior to the precipitation of the crystal phase. Most frequently the structure is formed at a temperature that is several degrees higher than the temperature of fuel consolidation.

The structure formed in a high-paraffinic fuel is rather easily destroyed because of the insignificant viscosity of the dispersion phase. Therefore the maximum pumpability temperature of such fuels, as a rule, is substantially lower than the consolidation temperature (Table 46).

In kerosenes used as fuels for jet engines this structure is more easily destroyed than in diesel fuels. For example, according to the data of Strauson [15] by slightly rocking the tank at a frequency equal to 6 cycles per minute for each 1/3° of cooling (thus simulating the motion of a fuel under the altitude changes taking place in the flight of an aircraft) made it possible to reduce the pumpability temperature

TABLE 46

Pumpability of Diesel Fuel Having a Solidification Temperature of $-30^{\circ}$ [14]

| 1 Число оборотов насоса в минуту | 2 Производительность насоса (в кг/час) при температуре, °С* | | | |
|---|---|---|---|---|
| | +10 | −30 | −40 | −50 |
| 500 | — | 540 | 535 | 258 |
| 3200 | 850 | 830 | 810 | 300 |

*Drop in pump output with a drop in temperature can be explained by the increase in fuel viscosity.

1) Pump rpm; 2) pump output (in kg/hr) at a temperature of °C *.

by $3^{\circ}$ for all of the fuels tested. Light rocking when applied to the operation of a pump of half the capacity serves to reduce the pumpability temperature of the fuels by $8\text{-}11^{\circ}$.

Depressor-type additives (see Chapter 14), restricting the formation of structures within the fuel, reduce the temperature at which the fuel-viscosity anomaly appears (Fig. 85) simultaneously with the drop in their solidification temperature and, consequently, the mobility (fluidity) of the fuels is improved.

## THE BEHAVIOR OF WATER IN FUEL AND THE BEHAVIOR OF WATER VAPORS IN THE INTAKE SYSTEM OF AN ENGINE

One of the factors responsible for the precipitation of the solid phase from fuels is the water that has been dissolved in the fuel or which has condensed from the air at the surface of a cold fuel. In both cases, the formation of the solid phase – crystals of ice – takes place directly within the fuel. Moreover, crystals of ice may come into the fuel from the outside in the form of rime coming off the walls of the tanks.

The crystals of ice in the fuel, moving together with the fuel through the fuel-feed system to the engine, can choke the filters, and

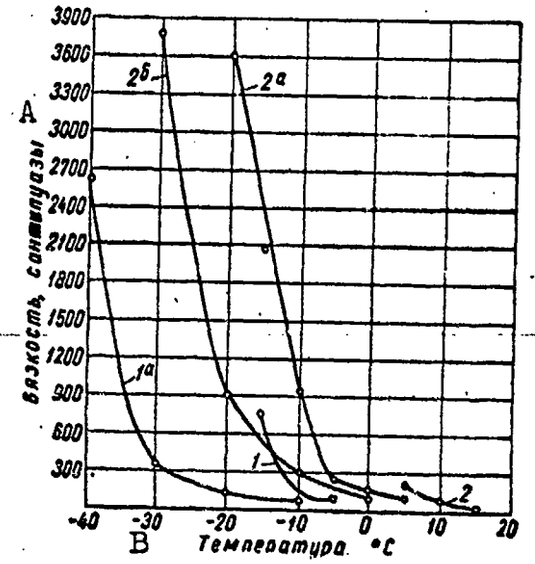


Fig. 85. Effect of paraflow on fuel viscosity. 1) Surakhany gas oil; 1a) Surakhany gas oil + 0.5% paraflow; 2) Emba solar distillate + Groznyy solar distillate (2:1); 2a) Emba solar distillate + Groznyy distillate (2:1) + 0.5% paraflow; 2b) Emba solar distillate + Groznyy solar distillate (2:1) + 1.5% paraflow; A) Viscosity, centipoises; B) temperature, °C.

this can result in the disruption of the fuel supply, and in the case of a great quantity of ice crystals the fuel supply can be entirely choked off. Ice crystals are particularly dangerous in aviation fuels.

Figure 86 illustrates how much the water dissolved in a fuel exerts an influence on the constriction of a filter with ice crystals. The greater the quantity of water dissolved in the fuel, the higher the temperature at which the fuel supply is reduced by 20% as a result of the choking of the filter with ice crystals.

It should be pointed out that given the same initial content of water dissolved in the fuel, depending on the cooling conditions, the design of the filter, and the design of the engine's fuel system, the temperature at which the filter becomes completely choked with ice crystals may vary within a very wide range. Therefore the curve in Fig. 6 characterizes only a general tendency, and this curve is typical only of certain specific cases. Under other conditions, the curve may lie substantially lower or higher without basically changing its shape.

The shapes and dimensions of the ice crystals in the fuel are functions of the conditions under which these ice crystals are formed [18]. In the absence of any mechanical impurities or fine fibers, tiny somewhat elongated ice crystals having dimensions of 4-10 μ are formed

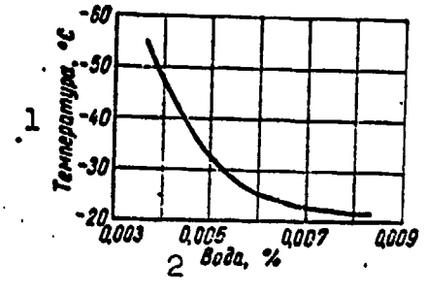


Fig. 86. Effect of dissolved water on temperature at which fuel supply is reduced by 20%. 1) Temperature, °C; 2) water, %.

in the case of rapid cooling, and these crystals range in dimension all the way to 15-40 μ in the case of slow cooling. In the presence of mechanical impurities long broken crystals (up to 1-4 cm) are formed, or a cotton-like fluffy mass is produced, and this floats in the fuel [19].

The small ice crystals that form in the fuel are reinforced with the passage of time, sometimes bringing about a change in the shape of the crystals. After pumping or mixing, the ice crystals may collect in the form of snow.

A unique "adsorption" of the fuel takes place on the surface of the ice crystals, and as a result the liquid that is formed after the melting of the crystal consists of two approximately equal-volume layers of water and fuel. In addition, some of the hydrocarbon components of the fuel, as well as the products of oxidation and polymerization under certain conditions associate with the water drops that are formed out of the fuel during cooling. At low temperatures these associated complexes also form crystals that are collected in the filter [20]. As a result of the "adsorption" of the fuel on the surface of the ice crystals and the formation of associated complexes, the volume of the crystal mass deposited in the filters increases by a factor of approximately two.

The rime deposited on the aircraft tank walls consists of ice crystals which "adsorb" fuel vapors; the fuel content here amounts to 60-80% [19].

Solubility of Water in Hydrocarbons and Fuels

All hydrocarbons are capable of dissolving small quantities of

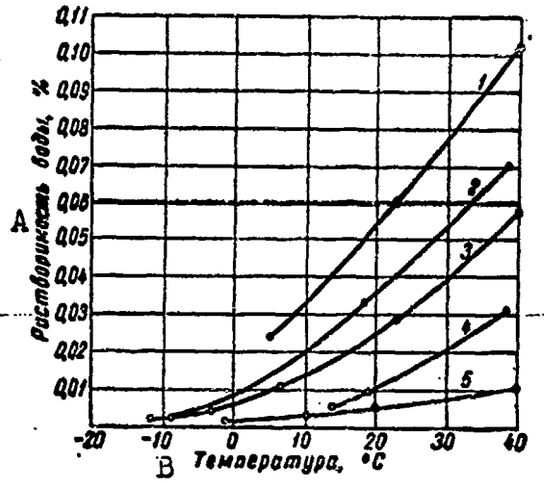


Fig. 87. Effective temperature on the solubility of water in hydrocarbons. 1) Benzene; 2) toluene; 3) xylene; 4) cyclohexane; 5) isooctane; A) solubility of water, %; B) temperature, °C.

water. The solubility of water depends on the structure of the hydrocarbon and on the temperature. The greatest quantity of water is dissolved in unsaturated hydrocarbons. The aromatic hydrocarbons are close to the unsaturated hydrocarbons in terms of solubility. The least amount of water is dissolved in the paraffinic hydrocarbons. With an increase in molecular weight, the solubility of hydrocarbons with respect to water diminishes, and this is particularly true in the case of aromatic hydrocarbons. With an increase in temperature, water solubility in hydrocarbons increases (Fig. 87), and again the increase is most significant in the case of aromatic hydrocarbons. The temperature relationship between water solubility in hydrocarbons can be expressed by the following empirical equation: $\log c = a - b/t$, which makes it possible to present this relationship in the form of a straight line.

The solubility of water in fuels is determined by the group hydrocarbon composition of the fuels. In fuels containing aromatic hydrocarbons, the solubility of water is greater.

The Effect of Various Factors on the Actual Quantity of Water Dissolved in Hydrocarbons and in Fuels

Solutions of water in hydrocarbons and fuel are extremely dilute in view of the limited solubility of water. As a result they are subject to the Henry law $C = KP$, where C is the concentration of the water in the hydrocarbon or fuel; P is the partial pressure of the water vapors;

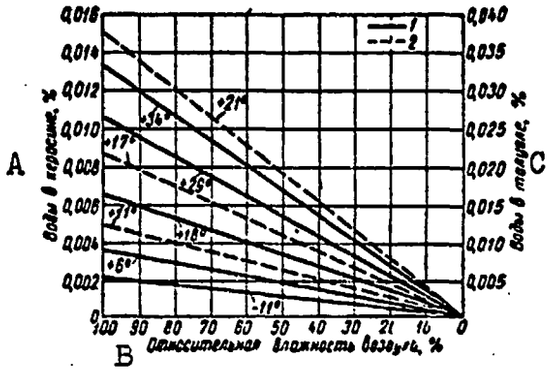


Fig. 88. Effect of relative air humidity on solubility of water and fuel. 1) Kerosene; 2) toluene; A) Water in kerosene, %; B) relative humidity of air, %; C) water in toluene, %.

K is the proportionality factor. It has been demonstrated [21] that $K = C_{maks}/P_v^{nas}$. In this case $C = C_{maks} P/P_v^{nas} = C_{maks} \psi$, where at the given temperature $C_{maks}$ is the maximum possible concentration of water in the hydrocarbon or fuel; $P_v^{nas}$ is the pressure of the saturated water vapors; $\psi$ is the relative humidity of the air.

Consequently, the concentration of water in the hydrocarbon or fuel, at constant temperature, is directly proportional to the relative humidity of the air. The validity of this relationship is confirmed experimentally with individual hydrocarbons, fuels of varying hydrocarbon composition, and oils [21]. Figure 88 illustrates the above-mentioned relationship.

Since the relative humidity of the air is not constant, neither is the content (quantity) of water dissolved in the fuel constant. With an increase in the relative humidity of the air, the fuel becomes saturated with the water from the air and the quantity of water dissolved in the fuel increases. With a reduction in the relative humidity of the air, the quantity of water in the fuel diminishes - we have the reverse transition of the water from the fuel to the air.

Consequently, the water dissolved in the fuel is in a state of equilibrium with the water contained in the air [19-24].

The cited formula is completely valid even in those cases in which the temperature of the fuel is higher or lower than the temperature of the air, and this is generally found to be the case under natural con-

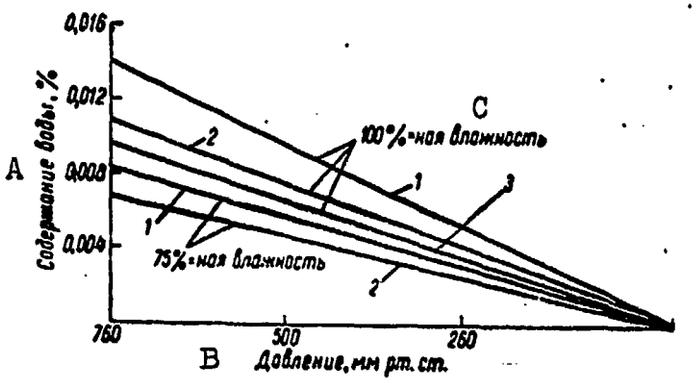


Fig. 89. Water content in fuel as a function of atmospheric pressure. 1) B-95/130; 2) TC-1; 3) T-1; A) Water content, %; B) pressure, mm Hg; C) 100% humidity.

ditions [25]. In this case $C_{maks}$ and $P_v^{nas}$ correspond to their values at the temperature of the fuel, and P corresponds to its value at the temperature of the air. Bu using this formula we can determine in advance the direction in which the content of the water dissolved in the fuel will change as the temperatures of the fuel and air (and the humidity of the latter) undergo change, and it will also be possible to determine the conditions under which condensation of water vapors from the air in the fuel can occur. Condensation of water vapors from the air in the fuel takes place when the fuel temperature is below the temperature of the air, and when the relative humidity of the latter (the air) attains a magnitude such that P exceeds $P_v^{nas}$, i.e., the relative humidity of the air, referred to the temperature of the fuel, exceeds 100%. Generally the conditions for such condensation of water vapors prevail with a pronounced increase in heat which is accompanied by a significant increase in the absolute humidity of the air. Given the simultaneous drop in the temperature of the fuel and air, as a rule, the content (quantity) of water dissolved in the fuel diminishes.

The content (quantity) of water dissolved in the fuel diminishes

also as the atmospheric pressure above the fuel is reduced (this occurs during aircraft takeoff). This relationship, as can be seen from Fig. 89, is independent of the relative humidity of the air and is rectilinear in character.

Speed of Change in Water Content in Hydrocarbons and Fuels

The speed with which the water content in the fuel changes is determined by the rate at which the water molecules are diffused from the fuel into the air or vice versa, by the rate at which the water molecules are diffused into the fuel, and also by the presence in the latter of convection flows; in addition, the rate of change in water content is determined by the ratio of the contact surface between the fuel and air to the volume of fuel poured into the container (tank).

The transition of the water molecules from the fuel into the air or vice versa takes place, as can be seen from the data presented in Table 47, virtually instantaneously. Within 1/2 a minute, given a fuel layer thickness of 5 mm, the water content in a fuel dried in advance, regardless of the initial value of the relative humidity of the air, attains its maximum possible value for the given humidity. Water leaves the fuel for dry air just as rapidly.

The diffusion of water in fuel takes place at a slower speed than the transition of the water from the fuel to the air or vice versa (Fig. 90). The rate of diffusion is determined by the difference in concentrations, and by the temperature and viscosity of the medium. The greater the difference in the concentrations of water in the various fuel layers, the higher the temperature and the lower the viscosity of the fuel, and the greater the diffusion rate for the water in the fuel.

With a drop in the fuel temperature, the viscosity of the fuel increases and this applies particularly to a high-boiling fuel. Moreover, with a drop in temperature the solubility of the water in the fuel

TABLE 47

Rate of Transition of Water from Air to Fuel and Back

(thickness of fuel layer, 5 mm; surface of contact between fuel and air, 21 $cm^2$; temperature, 18°)

| 1 Время насыщения и отдачи, мин. | 2 Содержание воды (в %) при относительной влажности воздуха | | | | | | |
|---|---|---|---|---|---|---|---|
| | 95% | | 65% | | 30% | | 2% |
| | | | 3 Топливо | | | | |
| | ТС-1 | Т-1 | ТС-1 | Т-1 | ТС-1 | Т-1 | ТС-1 |
| 4 Исходное топливо | 0 | 0 | 0 | 0 | 0 | 0 | 0,0109 |
| 1/2 | 0,0102 | 0,0093 | 0,0069 | 0,0062 | 0,0039 | 0,0031 | 0,0003 |
| 1 | 0,0098 | 0,0096 | 0,0073 | 0,0061 | 0,0038 | 0,0034 | 0,0002 |
| 3 | 0,0103 | 0,0090 | 0,0074 | 0,0065 | 0,0039 | 0,0033 | — |

1) Time of saturation and transfer, min; 2) water content (in %) at relative humidity of air; 3) fuel; 4) initial fuel.

diminishes and as a result there is a reduction in the maximum possible water-concentration difference in the various fuel layers. As a result the rate of water diffusion in the fuel, particularly in a high-boiling fuel, drops markedly. There is an increase in the speed with which the water content in the fuel changes as the ratio of the contact surface between the fuel and air to the fuel volume poured into the tank increases. Therefore, in horizontal containers ( tanks) and particularly in the case of incomplete filling of the container, the state of equilibrium between the water and the air is restored throughout the entire fuel volume more rapidly than in the case of vertical containers.

The convection flows that take place in the fuel as it is cooled or heated accelerate the shifting of the water in the fuel.

Conditions under which the Water is Separated from the Fuel in which it is Dissolved as well as the Conditions for the Formation of Ice Crystals

When the water content in the fuel exceeds the solubility of the

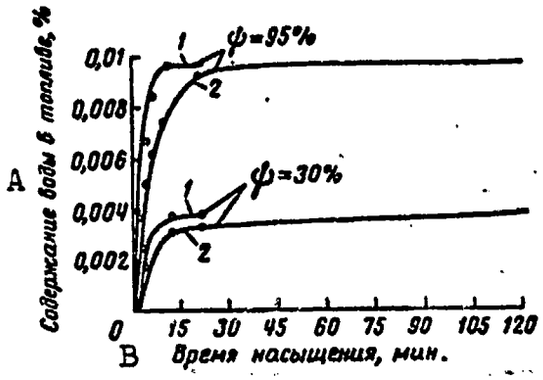


Fig. 90. Speed of water saturation of a dry fuel at various layer thicknesses. 1) Thickness of layer, 15 mm; 2) thickness of layer, 29 mm; A) Water content in fuel, %; B) saturation time, min.

water in the fuel for a given temperature, microdrops of water are separated from the fuel and the fuel becomes cloudy. This can take place both during the heating of the air, as well as in the case of air cooling. In the first case, the separation of these microdrops of water is observed when as a result of the rapid heating of the air the partial pressure of the water vapors in the air exceeds the pressure of the saturated water vapors at the temperature of the fuel (see page 312). If the container (tank) has not been completely filled with fuel, a relatively large quantity of water may be transferred to the fuel. In the case of cooling, conditions come about under which it is possible for the water to transfer from the fuel to the air. However, all of the excess water dissolved in the fuel does not always manage to make this transition to the air. If the cooling was rapid, and the conditions here were such that the quantity of the water dissolved in the fuel does not change too fast, a substantial portion of this water will not make this transition from the fuel to the air.* Since the solubility of the water in the fuel diminishes with a drop in the temperature of the fuel, the quantity (content) of water in the fuel, formerly situated in the lower part of the container, will exceed its solubility and the excess air will be separated from the fuel in the form of microdrops.

Microdrops of water may also be separated from the fuel in those cases in which, at constant air and fuel temperature, the relative humidity of the air is reduced. The state of equilibrium for the water

changes in a direction of reducing the quantity (content) of water in the fuel, and with a pronounced drop in the relative humidity of the air the excess water will again fail to make the transition to the air and will be separated from the fuel in the form of microdrops.

If the separation of the microdrops of water from the fuel takes place in any one of the above-enumerated methods, at a time at which the fuel is at a temperature below $0^{\circ}$, these microdrops will form microcrystals of ice. However, the separation of microdrops of water will not always be accompanied by the formation of microcrystals of ice in the case of negative temperatures. This can be explained by the capacity of the water drops to become supercooled and in this case as the dimensions of the drops diminish the degree of the water-drops' supercooling increases. The magnitude of the drop dimensions is determined by the rate of fuel cooling: the faster the fuel is cooled, the smaller the water drops and the greater their tendency to supercooling. The supercooled state is not stable, and therefore in the case of mixing or pumping a fuel containing supercooled drops of water, ice crystals are formed instantaneously. Not only the water separated from the fuel in the form of microdrops, but also the water contained in the dissolved state in the fuel, is capable of supercooling. For example, N.A. Ragozin [19] notes that with the gradual cooling of fuels containing a large quantity of aromatic hydrocarbons, the separation of the dissolved water from the fuel is delayed. Subsequently, with pronounced cooling of such supercooled fuel or during the mixing or pumping of such a fuel, the greater part of the water dissolved in the fuel is almost simultaneously separated out from the fuel, and this results in the subsequent formation of a large quantity of ice crystals.

The presence of ice crystals in the fuel may be the result of the falling, sliding, or washing down of the rime from the walls of the

containers and tanks carrying fuel on aircraft. Consequently, the ice crystals in a fuel may be formed both during a drop in fuel temperature as well as in the case of a rise in fuel temperature, and in individual cases ice may also be formed with a reduction in the relative humidity and pressure of the air above the fuel.

In the case of cooling, ice crystals are formed from the water dissolved in the fuel primarily with pronounced and substantial temperature differences taking place at high initial and final relative air humidities, in a more viscous fuel carried in horizontal containers which are completely filled, or in vertical containers which are filled to a sufficient height.

With slow cooling of the fuel, even in the case of high fuel viscosity and great thickness of the fuel layer in the container, and further given a limited surface of contact between the fuel and air (with complete filling of horizontal containers), the water may be able to achieve the transition to the air, as a result of which the solubility of the water in the fuel will not be exceeded and, consequently, no ice crystals will form.

With a sharp and substantial rise in the temperature of the air, ice crystals can form in the fuel from the rime on the walls of the containers. This can be observed primarily when the containers have not completely been filled with fuel.

Particularly favorable conditions for the formation of ice crystals prevail when the fuel is pumped from an underground container into a fuel truck. Fuel that has been stored in underground containers exhibits substantially higher temperature than the surrounding medium during the winter. During the pumping of the fuel into the fuel truck, there is a sudden drop in the temperature of the fuel, the solubility of the water in the fuel is reduced, and the excess of water cannot

make the transition to the air, thus being separated from the fuel in the form of microdrops which, as a result of the intensive mixing of the fuel, rapidly form ice crystals.

Method of Combating the Formation of Ice Crystals in a Fuel

There are a number of methods, both structural and physicochemical, to prevent the formation of ice crystals in a fuel or to eliminate ice crystals in a fuel. Among the structural methods we have the heating of the fuel or the utilization of a filter and the injection of isopropyl alcohol on the filter at the instant that the latter (the filter) becomes choked with ice crystals [26, 27]. Although both of these methods make it possible to prevent the choking of the filter with ice crystals quite effectively (heating) or to eliminate the formation of ice cry- in the filter (by the injection of alcohol), it is nevertheless necessary to have auxiliary equipment within the fuel system of the engine in order to heat the fuel or to provide for the alcohol injection and this is not desirable since it increases the weight of the aircraft.

The physicochemical method of preventing the formation of ice crystals in the fuel involves the addition of an additive (see Chapter 14) to the fuel. This additive increases the solubility of the water in the fuel and causes the dissolution of the ice crystals which enter the fuel from the outside, e.g., in the form of rime falling down from the walls of the container.

Behavior of the Water, Dissolved in Air, in the Intake System of the Engine

The basic mass of the liquid fuel in carburetor engines is vaporized within the carburetor itself. As a result of the intense vaporization of the fuel, the temperature of the combustible mixture is reduced by 15-25°. Simultaneously, there is a reduction in the temperature of individual component parts of the carburetor, in particular of the

throttle valve. As a result, the water dissolved in the air is condensed as this air passes into the carburetor, and at $-1^{\circ}$ and lower ice forms on the walls of the carburetor and primarily on the throttle (the entire top and the edges). Under particularly unfavorable conditions the icing of the throttle attains such a degree that it freezes completely and the engine comes to a stop. For more details about this see Chapter 17.

VAPORIZABILITY OF A FUEL AT LOW TEMPERATURES

The degree of fuel vaporization is determined by the pressure of the saturated fuel vapors. The higher the pressure of the saturated fuel vapors, the greater the degree of fuel vaporization and the easier it is to start a cold engine. With a drop in temperature, the pressure of the saturated fuel vapors is reduced. As can be seen from Fig. 91, the pressure of saturated vapors of an automotive gasoline drops from 400-500 mm Hg at $38^{\circ}$ to 30-40 mm Hg at $0^{\circ}$ and to 3-5 mm Hg at $-30^{\circ}$. The extent to which this has an effect on the starting of a cold engine is demonstrated by the data of L.A. Dem'yanov, presented in Fig. 92. While at $-5^{\circ}$ an engine operating on standard automotive gasoline can be started after 1-3 revolutions, at $-15^{\circ}$ no less than 15 revolutions are required in order to start a cold engine. Below $-15^{\circ}$ it is extremely difficult to start a cold engine unless special measures are implemented.

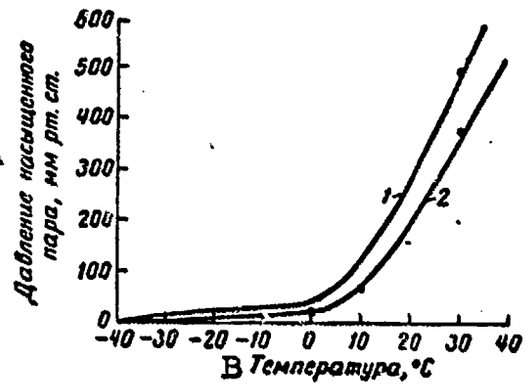


Fig. 91. Pressure of saturated gasoline vapors as a function of temperature. 1) Automotive gasoline No. 1; 2) automotive gasoline No. 2; A) Pressure of saturated vapor, mm Hg; B) temperature, $^{\circ}$C.

If the temperature of the surrounding air is low, even after the engine has been started, the gasoline will not always vaporize com-

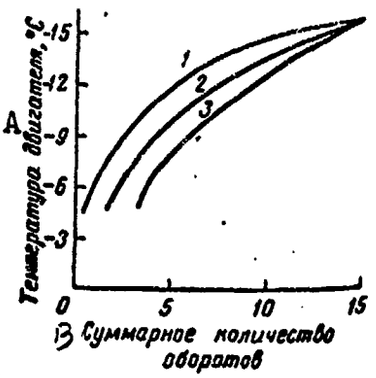


Fig. 92. Total number of engine rpm required to start the engine as a function of the temperature and speed of crankshaft rotation. 1) 50 rpm; 2) 40 rpm; 3) 30 rpm; A) Temperature of engine, °C; B) total number of revolutions.

pletely, particularly if the gasoline is one of a heavy-fraction composition.

The unvaporized portion of the fuel which enters the combustion chamber of an operating engine does not remain without change, but rather it oxidizes and forms peroxides, aldehydes, acids, and other oxygen-bearing compounds. In the case of extensive engine operation, products of oxidation collect in the liquid portion of the fuel and together with the unvaporized fuel enter the oil (lubricant), which is borne out by the high peroxide number of the oil, reaching as high as 10 units [33]. The quality of the oil is markedly impaired in this case.

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[Footnote]

316 At high relative air humidity.

## Chapter 12

## CORROSION PROPERTIES OF FUELS

The hydrocarbons that compose the basic part of petroleum-based and synthetic fuels, as well as fuels produced by semicoking and coking of coals, are quite inert toward all metals and alloys of metals used in machine building.

The naphthenic acids present in certain petroleums are distributed among the distillates on distillation of the petroleum in accordance with their boiling points. The benzene fractions contain virtually no naphthenic acids; the kerosene fractions are considerably richer in them, and the quantity of these acids again diminishes toward the gas-oil and solar (diesel) fractions.

The admissible quantity of naphthenic acids in commercial gasolines, kerosenes and diesel fuels is strictly limited by the corresponding technical specifications. Consequently, alkali treatment is applied to the corresponding distillates to remove them.

Commercial fuels contain only a quite negligible quantity of naphthenic acids that represents no danger as regards corrosion of elements of the engine's fuel system. Certain sulfur compounds present in the fuels may represent a real danger to the engine.

At the present time, the great mass of the petroleums extracted in the Soviet Union are sulfur-bearing petroleums and fuels (gasolines, kerosenes, diesel fuels and mazouts) with an elevated sulfur content are used in industry, agriculture and transportation in ever-increasing quantities, so that the problem of corrosive aggressiveness of the

fuels must be considered in connection with the nature and quantity of the sulfur compounds present in the fuel.

Sulfur compounds should be evaluated not only from the aspect of their corrosive action on metals, but also from the aspect of any possible influence that they might exert on the oxidation process of the fuels and the actual transformations in the oxidation process.

In speaking of the possible corrosive action of fuels, we should distinguish the corrosive activity of the fuels themselves from the corroding effects of their combustion products in thermal engines. These are two perfectly distinct aspects of the problem, each of which must be considered separately.

CORROSIVE PROPERTIES OF SULFUROUS FUELS

Sulfur-organic compounds present in a fuel may be regarded as corrosively aggressive components even at low temperature, although the extent of the aggressiveness is different for different compounds. Elimination of the most aggressive of them in the purification process at the plant makes the fuel practically safe from the standpoint of corrosion, although the quantity of other sulfur compounds left in it may still be considerable.

Corrosion of metals by sulfur compounds in a fuel is the result of direct chemical reaction between a sulfur-organic compound and the metal, with formation of the corresponding reaction products. According to Ya.B. Chertkov, fuels containing in one case 0.005% of elementary sulfur and 0.045% of α-phenylethyl mercaptan in the other, formed, at 120° in contact with bronze, residues whose compositions (in %) are presented in Table 48, i.e., copper sulfide formed in the first case and copper mercaptide in the second [1].

On combining copper with iron in hydrocarbon solutions of sulfur and hydrogen sulfide, L.G. Gindin and T.A. Miskinova did not observe

TABLE 48

Composition of Residues

| 1Топлива | 2Состав осадков, % | | | | |
|---|---|---|---|---|---|
| | C | H | O | Cu | S |
| 3 Керосин + 0,005% элементарной серы | 7,80 | 0,81 | 0,3 | 78,0 | 13,19 |
| 4 То же + 0,045% α-фенилэтилмеркаптана | 45,22 | 4,98 | 1,36 | 36,3 | 12,14 |

1) Fuel; 2) composition of residues, %; 3) kerosene + 0.005% of elementary sulfur; 4) same + 0.045% of α-phenylethyl mercaptan.

any signs of electrochemical corrosion [2]. However, it was established in experiments conducted by the author and L.A. Aleksandrova that in the case of contact between two metals (steel and copper, aluminum and brass) in a diesel-fuel medium containing from 0.18 to 1.60% of sulfur, clear signs of corrosion appeared on the metals after 3-4 days in the form of isolated dark spots and local color changes. When each of these metals was placed alone in the same fuels, such phenomena were not observed even after prolonged contact. Consequently, electrochemical phenomena are also observed here, although they are probably not of very great importance.

It is interesting to note one of the first observations to appear in the literature concerning the destructive action of sulfur compounds in the fuel on an engine's fuel system. A steel fuel line to a tractor engine that had been broken as a result of purely mechanical damage was replaced by a red copper tube. After 2 weeks, the copper tube had been destroyed by corrosion. Analysis of the tube material showed contents of 72.5% Cu, 5.0% C and 20.9% S. During 15 days' operation, 465 kg of kerosene containing 0.104% sulfur, i.e., 484 g, had flowed through this tube.

More or less profound breakdown of the metal and formation of

various types of deposits that are insoluble in the fuel may take place during the process of metal corrosion by sulfur-organic compounds in the fuel. Deposit formation is, of course, of greater importance than changes in the metal as regards ensuring reliable functioning of the fuel system. Moreover, corrosion can only formally be regarded in isolation from fuel-oxidation processes, which are accelerated by the metals and even more so by the products of corrosion. Under real conditions, all of these processes are intimately interwoven and influence each other reciprocally.

It has been established by prolonged stand and operational testing of sulfur-containing diesel fuels with sulfur contents below 1% that these fuels do not have any significant corrosive action on the fuel-feed apparatus of diesels. However, even though these tests were extended for 500-1000 hours, they were still not long enough to permit detection of even traces of corrosion on the engine components as a result of contact of these components with the sulfur-bearing fuel.

To ascertain the corrosive effect under the conditions of prolonged contact between metals and diesel fuels, M.S. Smirnov and Yu.V. Mikulin set up experiments in which plates of various metals (steel St. 3, steel 10, red copper and Br-S-30 lead bronze) remained in contact with fuel and fuel vapors for 2-3 years and longer at normal temperature. The fuel was held in glass vats covered with black paper to exclude the action of light. The results were evaluated by photographing the surfaces of the plates, inspecting them visually, and weighing them. Three fuels were compared: a low-sulfur fuel (0.18% sulfur) conforming to GOST 4749-49, a fuel with a 0.89% sulfur content in accordance with VTU 488-53 and an experimental fuel with a sulfur content of 1.25%.

The external appearance of the plates showed practically the same

changes for all fuels. Zones on which the color had changed – from yellow to green and blue – appeared on the steel; the copper showed uniform darkening or isolated spots of a cinnamon-brown color and poorly defined edges. The fuel containing 1.25% of sulfur produced indistinct dotted corrosion on all of the metals. Table 49 lists the changes in weight of the plates in $g/m^2$. The weight changes were of the same order of magnitude for the steel and copper in all fuels; only the lead bronze shows a considerably higher sensitivity to attack by sulfur compounds present in the fuel. Plates left in fuel vapors showed greater weight losses than the plates that had been totally immersed in fuel. This is evidently to be accounted for by the combined action of fuel vapors and atmospheric moisture.

TABLE 49

Corrosion of Metals by Fuels in Prolonged Contact at Normal Temperature

| 1 Металл | 2 Коррозия, г/м² | | | | | |
|---|---|---|---|---|---|---|
| | 3 топливо ГОСТ 4749-49 (S=0,18%, 3,5 года хранения) | | 6 топливо ВТУ 488-53 (S=0,89%, 3,5 года хранения | | 7 топливо опытное (S=1,25%, 2 года хранения) | |
| | в парах 4 | в жидкости 5 | в парах 4 | в жидкости 5 | в парах 4 | в жидкости 5 |
| 8 Сталь Ст. 3 | 2,14 | 1,54 | 2,34 | — | — | 4,00 |
| 9 Сталь 10 | 3,19 | 1,70 | 4,03 | 3,08 | — | 3,11 |
| 10 Красная Медь | 2,79 | 1,83 | 2,36 | 2,59 | — | 4,24 |
| 11 Бронза Бр-С-30 | — | 5,80 | — | 20,80 | — | 21,23 |

1) Metal; 2) corrosion, $g/m^2$; 3) fuel conforming to GOST 4749-49 (S = 0.18%, 3.5 years of storage); 4) in vapor; 5) in liquid; 6) fuel conforming to VTU 488-53 (S = 0.89%, 3.5 years of storage); 7) experimental fuel (S = 1.25%, 2 years of storage); 8) steel St. 3; 9) steel 10; 10) red copper; 11) Br-S-30 bronze.

The typical curves characterizing the kinetics of metal corrosion (Figs. 93 and 94) are of interest. In all cases, we observe a certain gain in the weight of the plates after the first few months as a result of formation of a sulfide or other film which then apparently peels

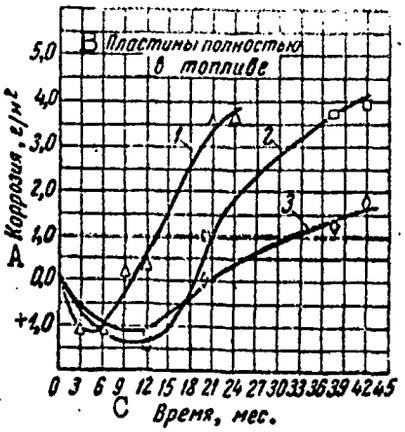


Fig. 93. Influence of fuel grade on corrosion of steel St. 3 plates. 1) Fuel with S = 1.25%; 2) fuel with S = 0.9%; 3) DS (GOST 4749-49). A) Corrosion, $g/m^2$; B) plates fully immersed in fuel; C) time, months.

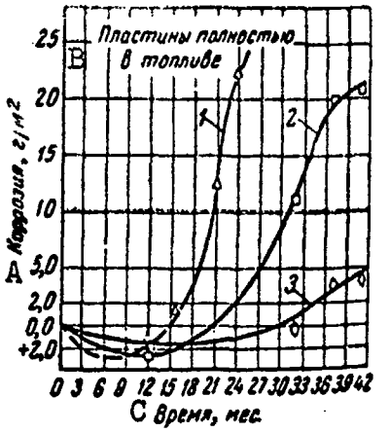


Fig. 94. Influence of fuel grade on corrosion of lead-bronze plates (key same as on Fig. 1 [sic]). A) Corrosion, $g/m^2$; B) plates totally immersed in fuel; C) time, months.

off or disperses in the fuel, with the result that the weight of the plates drops noticeably. A similar pattern was observed in the author's experiments to investigate the mechanism by which certain sulfur and phosphorus products act on metals – copper, cadmium and steel [3, 4].

Influence of Chemical Nature of Sulfur Compounds on Their Corrosion Properties

Schmidt [5] showed that elementary sulfur has a rather strong effect on Cu, Ag and Hg and a weaker action on other metals; hydrogen sulfide attacks Al, Zn, Cu, Ag, Fe and brass with formation of the corresponding sulfides. Similar conclusions were drawn from the results of studies conducted by Wood and Scheely [6].

Schmidt prepared a solution of isoamyl mercaptan in petroleum (sulfur content 0.29%) and treated copper, brass and silver with it at various temperatures and for various times. He found that mercaptides and sulfides formed. On addition of water and elevation of the temperature, corrosion was accelerated.

It was established by the same studies that other sulfur compounds – sulfides, disulfides, sulfoxides, sulfo acids, hydrogen sulfide and thiophene – exert no noticeable corrosive action on metals. Only in the presence of water and at elevated temperatures does corrosion begin to show.

Massing and Koch [7] demonstrated the corrosive action of elementary sulfur on nickel; with a 0.02% sulfur content in the fuel, the crystal structure of the nickel surface began to break up: the metal peeled.

On the basis of his investigations, Kiemstedt includes the following sulfur compounds among the corrosively aggressive types: elementary sulfur, hydrogen sulfide, mercaptans, sulfuric and sulfurous acids, sulfo acids and neutral and acid esters [8].

It follows from even these first experiments that elementary sulfur, hydrogen sulfide, and the mercaptans are the most aggressive sulfur compounds among those present in petroleum fuels.

A.S. Broun and A.P. Sivertsev [9] summarize the problem of the possible influence of sulfur compounds on an engine's fuel system in the following manner. They write that the most vulnerable points in the engine are its copper parts, particularly with respect to sulfur and hydrogen sulfide. Copper tubing is most sensitive to corrosion, and is followed by various copper-alloy components such as screens and the carburetor. The result is formation of a copper sulfide which, unfortunately, does not form a tough film like lead sulfide, and peels off after an extremely short time, to be carried away by subsequent portions of fuel and clog the fuel-feed system.

While hydrogen sulfide and elementary sulfur react rather rapidly with copper, the mercaptans are less active in this respect; thus, the mercaptans form only a slight iridescence on a polished copper surfa-

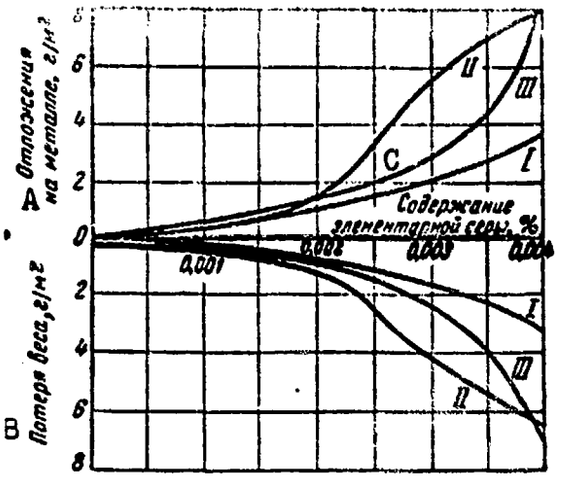


Fig. 95. Influence of elementary sulfur on corrosive aggressiveness of fuels. I) Baku kerosene; II) Grozny kerosene; III) kerosene produced from sulfurous petroleum. A) Deposition on metal, $g/m^2$; B) weight loss, $g/m^2$; C) elementary-sulfur content, %.

If, on the other hand, the fuel contains even traces of elementary sulfur in addition to the mercaptans, their action is intensified noticeably.

When mercaptans and elementary sulfur act jointly on copper, bright layers with different colors – red, green and so forth – form on its surface. Sulfur and hydrogen sulfide form a dull deposit on a copper surface; in its dry state, it resembles graphite. In the majority of cases, however, copper sulfide forms a steel-blue deposit. Addition of alcohol to a corrosively aggressive fuel intensifies corrosion, although only to an insignificant degree [9].

V.N. Zrelov [10] notes that when mercaptans are present in a fuel in quantities greater than 0.01% (reduced to sulfur), together with more than 0.002% of elementary sulfur, intensive corrosion of copper and copper alloys accompanied by formation of deposits that adhere to the metals and solid residues that are not soluble in the fuel is ob-

served in the engine's fuel system at 120°.

Figure 95 shows the results of experiments with kerosenes of various origins to which elementary sulfur had been added. It may be seen that the corrosive effect with respect to bronze, which is insignificant for elementary-sulfur contents lower than 0.002% in the fuel, increases sharply as the content of sulfur is further increased. Simultaneously, the quantity of deposit noted in the fuel increases; this is copper sulfide [10].

The formation of gelatinous deposits in the fuel systems of engines operating on sulfur-containing fuels is regarded by a number of foreign authors as the result of a reaction between the mercaptans present in the fuel with the copper or copper alloys from which the fuel-system components are made. It is emphasized that disulfides do not form such deposits at normal working temperatures. These gelatinous deposits do not dissolve in ordinary solvents and, as a result, can be eliminated from the fuel system only manually after disassembly of the entire device.

Analysis has shown that these deposits, which resemble lubricating greases, consist basically of the fuel, products of its oxidation, and copper mercaptide, which acts as a thickener. Water is a persistent component of such deposits. A typical composition of the deposits (in % by weight) is as follows.

| | |
|---|---|
| Fuel | 95.0 |
| Copper mercaptide | 1.8 |
| Oxidation products | 2.2 |
| Water | 1.0 |

The copper mercaptide isolated from the deposit had the following elementary composition: $C_{12}H_{21}SCu$.

The investigations were carried out on a laboratory machine in

which the fuel circulated for 2 weeks through a filter with a metallic (bronze, brass or copper) screen. At the end of the test, the filter was treated with acid, followed by titration of the mercaptide that had been separated in order to determine the weight of the copper mercaptide that had formed.

The following interesting conclusions were drawn [11].

1. All mercaptides present in the fuels form copper mercaptides under appropriate conditions.

2. At normal working temperatures, the disulfides do not form the gelatinous deposits described above.

3. The largest quantity of deposits is obtained, all other conditions the same, on brass and bronze filters. The deposits formed on copper filters represent 1/4 to 1/6 this amount.

4. For a given high mercaptan content, direct-distilled fuels form smaller quantities of deposits than fuels produced by cracking.

5. The largest quantities of deposits are obtained in mixtures of mercaptan-containing fuels from direct distillation and catalytic cracking. In this case, the quantity of gelatinous deposits is at least 2 times as great as the sum of the deposits obtained in each of the fuels used alone.

6. Even when present in small quantities, water contributes to the formation of the gelatinous deposits described above. Distilled water has this property to the lowest degree, while water containing free alkali manifests it most strongly. Sea water occupies an intermediate position in this respect. In general, the higher the pH of the water, the more aggressive will it be as regards deposit formation.

Tests of a number of fuels under operational conditions fully confirmed the results of laboratory investigations, the only difference being that 3-4 times as much of the deposits was formed in a given

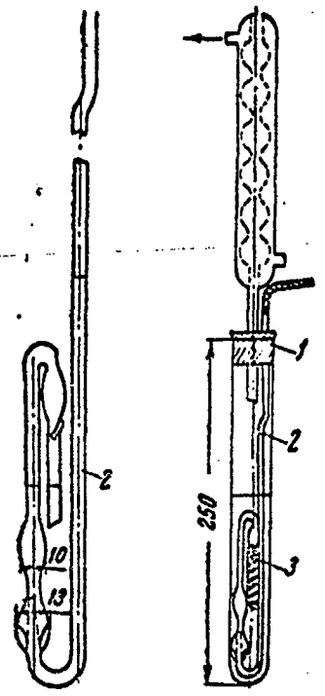


Fig. 96. Apparatus for determining corrosion aggressiveness of fuels. 1) Test tube; 2) tubing; 3) metallic plate.

period of time during operation than in the laboratory.

Yu.V. Snitserov, V.S. Demchenko, and A.S. Gorshenin made investigations of a number of fuels by a method which they developed, using the instrument shown in Fig. 96. 100 ml of the fuel to be tested were poured into a test tube having a tube injector with a 40 x 10 x x 2-mm metallic plate suspended from it. The plates were first polished, washed in benzene, dried and weighed. During the experiment, the plates were continuously washed with a fuel-and-air emulsion.

Table 50 shows the total and mercaptan sulfur contents in the fuel specimens tested, while Fig. 97 shows the results of tests of fuel specimens on VB-24 bronze at 120° with a 20-25-ml/min supply of air.

Fuel No. 5, which contains the largest quantity of mercaptans, produced the most rapid corrosion; however, fuel No. 1, with its small total sulfur content and negligibly small mercaptan content was directly behind it in corrosive aggressiveness. Together with this, the experimental fuel (specimen 8) produced very little corrosion in spite of its very high total sulfur and mercaptan content. The above indicates that the sulfur content and, in particular, the mercaptan content in a fuel (when the structure of the latter is unknown) are not sufficient to characterize the corrosive aggressiveness of a fuel.

I.Ye. Bespolov et al [12] studied the corrosive effects of TS-1 and T-2 fuels containing from 0.12 to 0.30% of total sulfur and from

TABLE 50

Characterization of Test Fuels

| 1 Показатели | 2 № образца | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 3 Марка топлива . . . | 4 ТС-1 | 4 ТС-1 | Т-2 | Т-2 | 4 ТС-1 | Т-4 | Т-1 | 5 Опытный |
| 6 Содержание серы, % | 0,123 | 0,120 | 0,154 | 0,153 | 0,247 | 0,210 | 0,123 | 0,660 |
| 7 Меркаптановая сера, % . . . . . | 0,0008 | 0,0030 | 0,0034 | Нет 8 | 0,040 | 0,010 | 0,0007 | 0,021 |

1) Index; 2) specimen No.; 3) type of fuel; 4) TS-1; 5) experimental; 6) sulfur content, %; 7) mercaptan sulfur, %; 8) none.

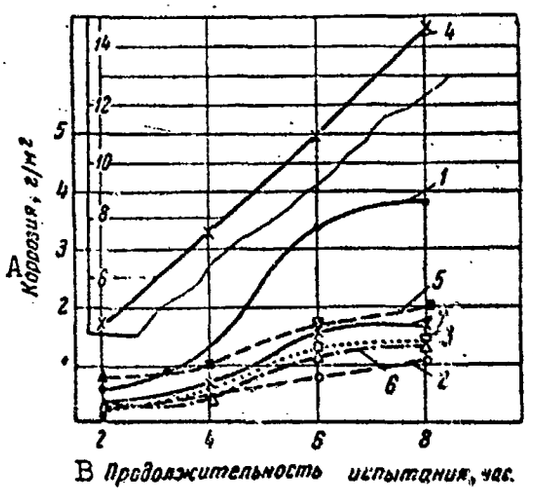


Fig. 97. Influence of mercaptan and elementary-sulfur contents in fuels on corrosion of VB-24 bronze. 1) TS-1; 2) T-2; 3) T-2; 4) TS-1; 5) T-4; 6) T-1; 7) experimental. A) Corrosion, $g/m^2$; B) duration of test, hours.

0.002 to 0.05% of mercaptans on copper and VB-24 bronze at 60° over a period of 100 hours. The experiments showed that the corrosive aggressiveness of fuels TS-1 and T-2 toward bronze when they contain less than 0.01% of mercaptans is approximately the same. With higher mercaptan contents (from 0.02% to 0.050%), the aggressiveness of T-2 fuel is higher than that of TS-1. This higher aggressiveness of T-2 fuel was also observed in the experiments with copper. The authors show by direct experiment that this is connected with the presence of low-molecular-

weight mercaptans in T-2 fuel (with its broad fractional composition), these compounds being absent in TS-1 fuel.

TABLE 51

Corrosion of Nonferrous Metals and Alloys in Fuels for VRD

| 1 Материал | 2 Коррозия в керосине, мг/10 см² | |
|---|---|---|
| | 3 прямой перегонки | 4 термического крекинга |
| 5 Бронза | 3,8 | 5,4 |
| 6 Кадмий | 1,8 | 1,1 |
| 7 Цинк | 1,0 | 0,8 |

1) Material; 2) corrosion in kerosene, mg/10 $cm^2$; 3) direct-distillation; 4) thermal-cracking; 5) bronze; 6) cadmium; 7) zinc.

Special experiments with the specimens showed that on addition of up to 0.002% of sulfur (a quantity not detected by the copper-plate test; GOST 6321-52) to TS-1 fuel containing 0.018% of mercaptan sulfur, its corrosive action on bronze was not intensified, while that on copper was intensified considerably. Even when 0.001% of sulfur was added to the fuel, the corrosion of copper was increased by a factor of 18. The corrosion was accompanied by a reduction in the mercaptan content in the fuels; here, this process continues in time up to complete exhaustion of all mercaptans present in the fuel.

The results of an investigation of the corrosive action of fuel sulfur compounds on cadmium are of interest. Cadmium coatings are used extensively in fuel-pump parts for jet and other gas-turbine engines.

B.A. Englin et al [13] investigated the corrosive action of fuels containing various quantities of mercaptans on cadmium-plated steel barostat springs. Fuels with the following mercaptan contents (in %) were tested.

| | |
|---|---|
| TS-1 | 0.047 |
| T-2 | 0.052 |
| Cracking kerosene | 0.059 |
| TS-1 | 0.005 |
| T-1 | 0.0003 |

The fuels contained from 0.0004 to 0.0143% of water (ordinary fuels contain from 0.003 to 0.008% of water). The springs were in contact with the fuel for 10 days at operating temperature. The changes in the external appearance of the fuel and the springs, the change in weight of the springs and the presence of deposits were evaluated.

There was no deposit in any of the dehydrated fuel specimens (water from 0.0004 to 0.0012%); the fuel was clear; the external appearance of the spring had not changed. In TS-1 (0.005% of mercaptans) and T-1 (0.0003% mercaptans) fuels, the same pattern was observed in the presence of 0.0046 to 0.0109% of water. In TS-1 and T-2 fuels with 0.047% and 0.052% of mercaptans, respectively, with natural moisture (0.0054-0.0063% of water) and artificially moistened specimens (0.0098-0.0110% of water), deposits had formed after 1-3 days of contact. A decrease in the mercaptan content in the fuels was established in these cases by direct determination. Analysis of the deposit showed 40.69% C, 8.19% H, 8.55% S, 12.27% O and 30.3% of ash, the latter containing 43.75% Cd, 10% Si, 7.5% Cu, etc. Consequently, a distinctly expressed corrosion process is in evidence here.

These experiments were repeated by I.Ye. Bespolov and co-authors on cadmium-plated springs with and without chromatic passivation. In the absence of passivation, gelatinous deposits formed, particularly in cases of moist fuel. The mercaptide isolated from the deposit (28.5% content therein) had the composition 46.7% C, 8.5% H, 16.3% S, 28.5% Cd. The use of chromatic passivation raises the corrosion resistance

of the cadmium coatings noticeably [12].

A cracking kerosene that contained 0.059% of mercaptans did not show any corrosive effect on cadmium in the experiments of B.A. Englin. In the opinion of the authors, this indicates an aromatic nature for the mercaptans in the cracking kerosene, which, unlike aliphatic mercaptans, possess a protective anticorrosive action. The authors account for the damage to the cadmium surface, with formation of gelatinous deposits, by the presence of largely aliphatic mercaptans and water in the fuel.

Statements as to the elevated corrosive aggressiveness of aliphatic mercaptans as compared with the aromatics are encountered in many reports, although there are also data that contradict this affirmation. In investigating the corrosive aggressiveness of cracking and direct-distilled kerosenes, Ya.B. Chertkov [1] obtained the data listed in Table 51.

Bronze corrodes more severely in thermal-cracking kerosene than in direct-distilled kerosene, while zinc corrodes almost equally in either.

The literature contains data attesting to the ability of aromatic mercaptans to inhibit the fuel-oxidation process in the presence of metals. It is noted in other cases that the presence of an oxidation-promoting or antioxidant effect of aromatic and aliphatic mercaptans depends on their concentrations in the fuel.

Proceeding from the premises developed by the author in connection with research into the mechanism by which anticorrosive sulfur- and phosphorus-containing oil additives act [3, 4], it may be assumed that aliphatic and aromatic mercaptans are aggressive toward copper and other nonferrous metals, although the mercaptides that form are not attached to the metal with the same tenacity. As a result, rapid peel-

ing of the film that has formed takes place in some cases, so that new zones of the metal's surface are exposed for corrosion, while in other cases the film that has formed adheres tenaciously to the surface, thereby preventing further progress in the corrosion process.

The experiments of S.E. Kreyn and G.S. Tarmanyan brought to light the high anticorrosion properties of phenylethylmercaptan with respect to lead and lead bronze. If such a film forms rapidly enough, the results include passivation of the metal surface, i.e., it ceases to exert its catalytic effect on the fuel-oxidation process [4].

B.V. Losikov showed that elementary sulfur present in the colloidally dissolved state in sulfuretted oil forms a sulfide film very rapidly and even at moderate temperatures on metals (copper, cadmium, lead). This film possesses a distinctly expressed passivating action, although its strength is not particularly high; it is easily removed from the surface, exposing a new fresh surface to corrosion. It is precisely for this reason that sulfuretted oil has been found almost ineffective [16, 17, 3, 4] as an anticorrosive additive component. It might be supposed that the result of the combined action of elementary sulfur and mercaptans observed by the present authors is determined not only by the nature of the latter and the metals, but also by their concentration in the fuel and the external conditions – temperature, time of contact, and nature of mechanical disturbances. This is obviously the reason for the lack of agreement in evaluations of the comparative corrosive aggressiveness of different types of mercaptans.

These remarks do not deprecate the importance of the unquestionable fact that elementary sulfur and mercaptans are the most aggressive components among the sulfur compounds of petroleum fuels and that their aggressiveness is manifested even at extremely low concentrations in the fuel. Together with this, as we have already noted, cases are ob-

served in which fuels – even fuels containing no perceptible quantities of elementary sulfur or mercaptans – exert a clear-cut corrosive action on metals. This is most often the case with high total sulfur contents, but it sometimes occurs even with relatively small contents.

B.P. Kitskiy [18] reports that during a 150-hour test of an engine on a gasoline containing 0.15% of sulfur and not having the property of darkening a copper plate, the nozzle throughput increased by 8% as a result of corrosive wear.

Comparative Resistance of Metals to Corrosion by Sulfur Compounds in Fuels and the Influence of External Factors on Corrosion

As we noted above, nonferrous metals – copper and its alloys, cadmium, lead, zinc and silver – are most susceptible to corrosion by sulfur compounds in fuels. Copper is evidently more resistant to corrosion than its alloys (certain bronzes). Iron and particularly unalloyed and alloyed steels are regarded as virtually immune to attack by sulfur compounds. An example that illustrates the differences between the corrosion resistances of metals may be found in the data of Yu.V. Snitserov et al as listed in Table 52. The comparative resistances of various metals may be judged from the figures listed in Table 51.

But it would appear hardly possible to construct a scale in which the metals are arrayed in order to their resistance to corrosion by sulfur compounds. In the general case, this will depend on the nature of the sulfur compounds and their concentration in the fuel, and upon external conditions – temperature, presence or absence of moisture, extent of aeration of the fuel, and so forth.

The fact that numerous tests and long-term operation on diesel fuels with sulfur contents less than 1% have not turned up a single case of corrosion of the fuel apparatus (plunger pairs, nozzle-atomizer needles) by the fuels, even though the atomizer needles, for example,

TABLE 52

Comparative Resistances of Certain Metals to Corrosion (in $g/m^2$) by Sulfur Compounds*

| 1 Сплавы | 2 ТС-1 (обр. 1) | | 5 Т-2 (обр. 3) | |
|---|---|---|---|---|
| | 3 с воздухом 25—50 мл/мин | 4 без воздуха | 3 с воздухом 25—50 мл/мин | 4 без воздуха |
| 6 Сталь 12ХН3А . . . . . | 7 Нет | Нет | Нет | Нет |
| 8 Бронза ВБ-24 НЦ . . . . . | 0,75 | 0,25 | — | — |
| 9 Медь электролитическая . . . . | 1,03 | 0,89 | 0,56 | 0,43 |
| 10 Бронза ВБ-24 . . . . . | 3,36 | 1,36 | 0,78 | 0,74 |
| 11 Свинец С-1 . . . . . | 7,65 | 3,61 | 2,26 | 2,35 |

*For numbers assigned to fuels see Table 50. Experimental conditions: temperature 120°, time 6 hours.

1) Alloy; 2) TS-1 (specimen 1); 3) with air, 25-50 ml/min; 4) without air; 5) T-2 (specimen 3); 6) steel 12KhN3A; 7) none; 8) bronze VB-24 NTs; 9) electrolytic copper; 10) VB-24 bronze; 11) lead S-1.

operate under conditions of elevated temperature, attests to the high resistance of steels to the corrosive effects of sulfur-containing fuels. Corrosion of diesel-engine fuel apparatus is not observed even when fuels with even higher sulfur contents (1.25% and even 1.60%) are used in them.

M.S. Smirnov and V.N. Dneprov [19] conducted long-term tests to determine the wear of plunger pairs in diesel fuel pumps during operation on fuels with various (below 1.25%) sulfur contents; these did not indicate any difference in plunger wear in operation on low-sulfur and high-sulfur fuels. It should be noted, however, that all fuels under discussion here contained relatively low mercaptan contents (0.006-0.008%), a property that is, generally speaking, typical for diesel fuels.

Tests conducted by the same authors on the motorless stand shown in Fig. 98, which was equipped with radioactive (irradiated) plunger pairs, made it possible to detect certain differences in plunger wear,

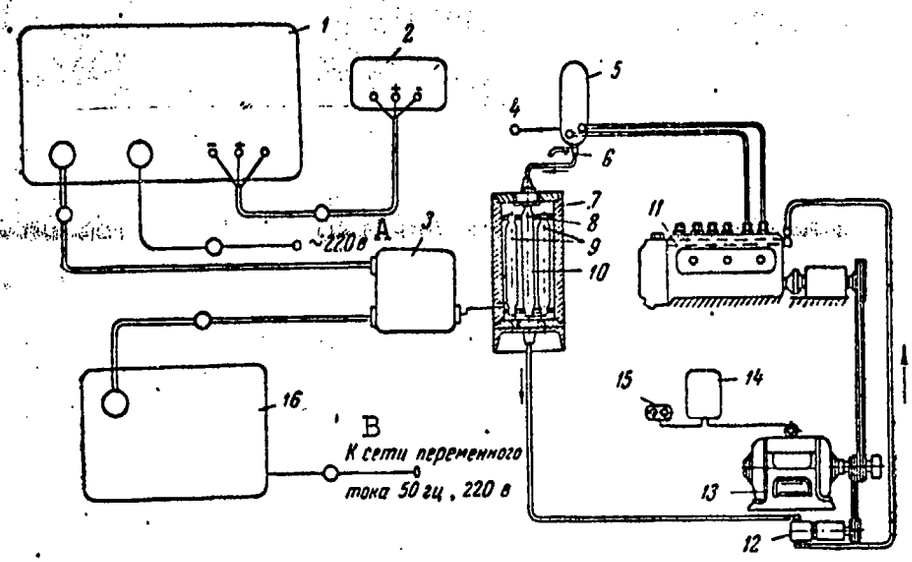


Fig. 98. Diagram of apparatus for estimating wear on plunger pairs by radioactive-isotope method. 1) Conversion unit; 2) mechanical counter; 3) input unit; 4) air thermometer; 5) reservoir; 6) cock for withdrawal of samples; 7) lead housing; 8) counter-tube unit; 9) counter tubes; 10) glass tube in line; 11) six-plunger fuel pump to ZD-6 engine; 12) BNK booster pump; 13) electric motor; 14) electric motor starter; 15) start button; 16) rectifier. A) 220 vAC; B) to 50-cycle 220 v AC line.

TABLE 53

Influence of Temperature on Rate of Corrosion (fuel 1 after Table 50)

| | 1 Коррозия (в г/м²) при температуре (в °С) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 100 | | 120 | | | | 140 | |
| | 2 и продолжительность испытания, часы | | | | | | | |
| | 6 | 8 | 2 | 4 | 6 | 8 | 4 | 6 |
| 3 Бронза ВБ-24 . . . . . | 0,33 | 0,69 | 0,58 | 1,28 | 3,36 | 3,73 | 1,65 | 4,67 |
| 4 Медь электролитическая | 0,12 | 0,32 | 0,38 | 0,65 | 1,03 | 1,39 | 0,88 | 1,18 |

1) Corrosion (in $g/m^2$) at temperature of (in °C); 2) and test time in hours; 3) bronze VB-24; 4) electrolytic copper.

at least for a fuel containing 0.025% of mercaptans and the same fuel after elimination of the mercaptans. The results of these experiments are listed in Fig. 99. Here, curve 1 refers to the low-sulfur fuel,

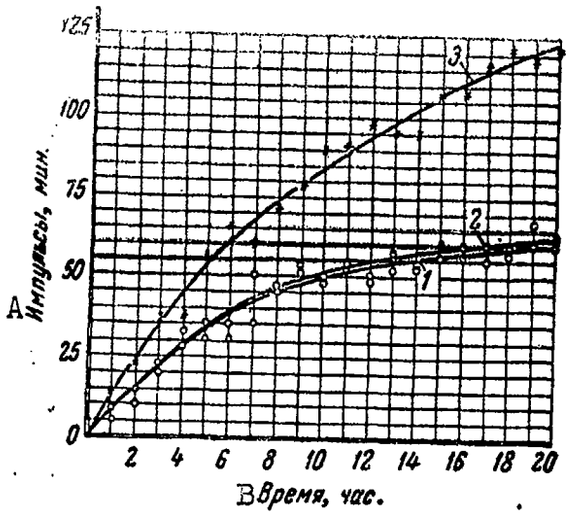


Fig. 99. Influence of mercaptan content in diesel fuel on plunger wear. 1) Standard diesel fuel; 2) high-sulfur diesel fuel without mercaptans; 3) high-sulfur diesel fuel with mercaptans. A) Impulses, min [sic]; B) time, hours.

which contained 0.18% of sulfur, curve 3 to the high-sulfur fuel containing 1.0% of sulfur, of which 0.025% was mercaptan sulfur, and curve 2 to the same fuel after complete elimination of the mercaptans. Although no corrosion damage whatsoever could be detected in this case on the surfaces of the plungers and sleeves, the data obtained nevertheless testified convincingly to the ability of mercaptans to intensify plunger wear to a certain degree, obviously through corrosion processes.

The intensity of corrosion increases sharply with increasing temperature. This may be seen from Table 53 (after Yu.V. Snitserov et al).

Particular attention must be paid to this when the fuels are used in the engines of supersonic aircraft, and in any other engine where the fuel may be subject to heating or the actual components of the fuel system operate under conditions of elevated temperature.

Corrosion of metals by aggressive sulfur compounds is intensified in the presence of water, as illustrated by the examples given earlier.

It is evident that the presence of air also accelerates the progress of corrosion.

Not only (and not so much) prevention of corrosion of the fuel-system elements, but also prevention of formation of corrosion deposits on their surfaces are of great importance in ensuring normal operation of a modern engine's fuel system. Such deposits, which take the form of dense resinous layers, form chiefly on nonferrous metals – cadmium, zinc and particularly bronze. Such deposits are not formed on steels. The basic cause of their formation is the presence of elementary sulfur and mercaptans in the fuel. Other sulfur compounds – aliphatic and aromatic sulfides and disulfides, as well as thiophene and thiophane – form no corrosion deposits on metals.

CORROSIVE PROPERTIES OF COMBUSTION PRODUCTS OF SULFUR FUELS

Under conditions of the thermal-engine cycle, sulfur-organic compounds of any structure form the sulfur oxides $SO_2$ and $SO_3$ in addition to the products of oxidation of carbon and hydrogen as a result of combustion.

The formation of $SO_2$ in the combustion products has always been unquestioned, while the presence of $SO_3$ in the same products required direct experimental confirmation.

In the production of sulfuric acid, oxidation of $SO_2$ into $SO_3$ does not take place readily, but requires creation of special conditions – those of directional catalysis. The extent to which conditions in the firebox of boiler installations or in the combustion chambers of gas turbines and internal-combustion engines may contribute to this reaction remained unknown.

One of the first indications of the presence of $SO_3$ among the combustion products of sulfur fuels in diesels is due to Cloud and Blackwood [24]. In experiments run on three internal-combustion engines of

different types, the authors noted that from 60 to 90% of all the sulfur present in the fuel formed $SO_3$ on combustion. These experiments indicated that $SO_2$ did not produce such grave consequences as $SO_3$, the action of which resulted in accelerated wear and in the formation of varnishes on the piston and cylinder walls.

The results of these experiments were discussed later in a number of reports [20-22]. The opinion was expressed that although the formation of $SO_3$ in combustion of high-sulfur fuels may be regarded as established beyond question, there remains doubt as to whether the quantity of $SO_3$ is actually as large as has been stated. An analysis of exhaust gases carried out by a number of investigators showed that the percentage content of $SO_3$ detected in them depends to a major degree on the point at which the gas sample was taken and the method used in taking it. Here the hypothesis was advanced that conversion of the lower oxide into the higher is possible as a result of the catalytic action of the metallic surfaces and, consequently, may take place not only on the walls of the cylinder sleeve and piston, where this reaction is least desirable, but also on the path from the combustion chamber to the point at which the sample was withdrawn. For this reason, analysis of the gas for its $SO_2$ and $SO_3$ contents – no matter where the gas sample was taken – does not give a complete conception of the actual scales on which the higher oxide of sulfur is formed [25]. Nevertheless, the presence of both $SO_2$ and $SO_3$ in the combustion products of high-sulfur fuels need not be questioned.

The corrosive action of sulfur oxides on metals may be manifested under two essentially different sets of conditions: 1) at low and moderate temperatures and 2) at high temperatures. In the former case, we shall be dealing with low-temperature corrosion and in the latter case with high-temperature corrosion.

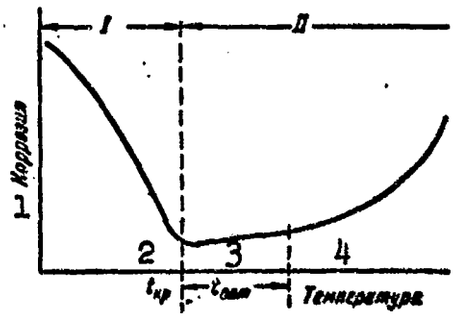


Fig. 100. Combustion-chamber corrosion as a function of temperature of corroded surface. 1) Corrosion; 2) $t_{kr}$; 3) $t_{opt}$; 4) temperature.

L.V. Malyavinskiy and I.A. Chernov [26] present a typical curve of combustion-chamber corrosion as a function of the temperature of the surface being corroded (Fig. 100). Here I is the region of electrochemical corrosion taking place under an extremely thin adsorption or visible film of electrolyte, and II is the region of dry chemical gas corrosion.

The possibility and intensity of vapor condensation onto the surface at a given water-vapor concentration in the combustion products depends on the surface temperature. If the temperature is above the critical ($t_{kr}$), i.e., above the "dew point," no condensation occurs. As the temperature of the surface diminishes, the possibility of condensation increases.

As is indicated by the curve in Fig. 100, the rate of electrochemical corrosion increases sharply with diminishing temperature. The rate of gaseous corrosion increases with diminishing temperature, but not very fast. The specific importance of electrochemical and chemical corrosion depends on the device in which the fuel is burned and the conditions under which it burns, but, as a rule, low-temperature electrochemical corrosion is the greater danger in internal-combustion engines and in the boilers of steam installations.

Let us consider this problem in greater detail as it applies to the case of sulfur-fuel combustion.

As we have already stated, the initial product of fuel-sulfur combustion is sulfur dioxide, which, reacting with the excess of oxygen always present in the boiler or combustion chamber, is oxidized t:

sulfur anhydride in accordance with the equation

$$SO_2 + {}^1/_2O_2 \rightleftarrows SO_3.$$

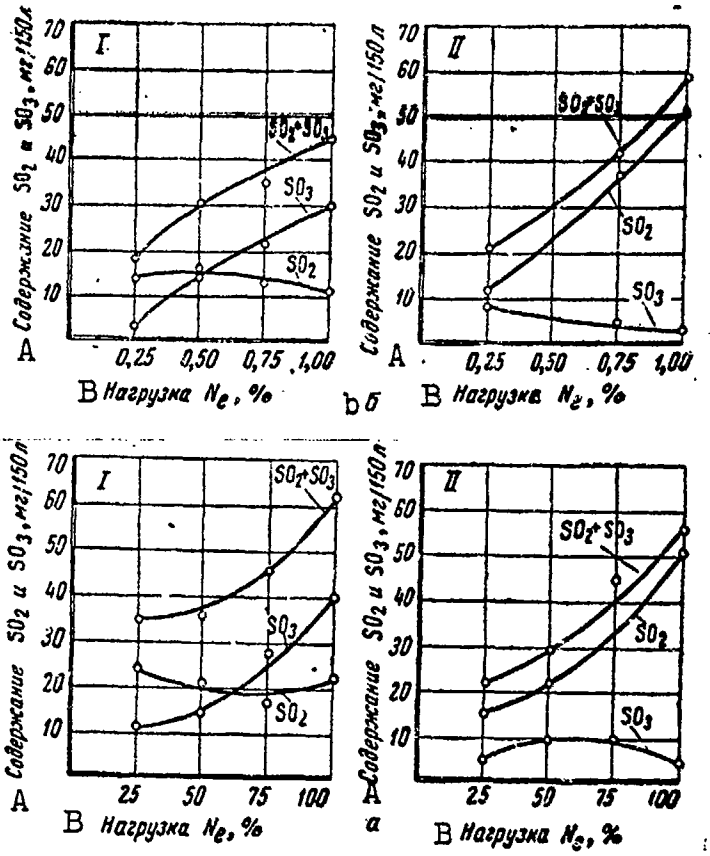


Fig. 101. Influence of ammonia on $SO_2$ and $SO_3$ contents in exhaust gases. a) 2Ch-8.5/11 engine (fuel with S = 1.25%); b) 1Ch-10.5/13 engine (fuel with S = 1.6%). I) Without addition of ammonia; II) with delivery of 3 liters/hour of ammonia. A) Content of $SO_2$ and $SO_3$, mg/150 liters; B) load $N_e$, %.

Given adequate time, this reaction proceeds until an equilibrium has been reached; this depends on the partial pressures of the sulfur dioxide and oxygen and on the temperature of the gases [27].

Adequate data are not available on the question of the rate of the reaction in which $SO_2$ oxidizes to $SO_3$ under the conditions of thermal engines; however, it may apparently be assumed that the rate of the reaction increases with rising temperature over a broad temperature range. An indirect but convincing piece of evidence in favor of

Fig. 102. Saturation line and dew points of mixture of $H_2O + H_2SO_4$ for total pressure. 1) Superheated vapor; 2) dew line; 3) moist vapor; 4) boiling line; 5) liquid.

this is presented by the data of Fig. 101, a and b, which were obtained by L.A. Aleksandrova in simultaneous determination of the quantities of $SO_2$ and $SO_3$ in the exhaust gases of diesels operating on a fuel containing 1.25% and 1.60% of sulfur. It may be seen that raising the load on the engine, which always involves a rise in the cycle temperature, results in a consistent increase in the fraction of $SO_3$ in the combustion products of the high-sulfur fuel.

Under any constant set of conditions (excess of air, fuel-feed rate) and gas temperature T, the quantity of $SO_3$ formed during a time $\tau$ will be equal to

$$[SO_3] = f(T, \tau).$$

The formation of sulfuric anhydride in the combustion products is reflected in the $t_{kr}$ – the temperature at which condensation begins on the surfaces in contact with the gas.

Since the vapor pressure of sulfuric acid is considerably lower than that of water at a given temperature, the dew point (the temperature at which condensation begins) for it will be considerably higher than might be expected solely on the basis of the water-vapor content in the gases.

Sulfuric anhydride forms sulfuric-acid vapor of the corresponding concentration on reaction with the water vapor in the combustion products. As a result, a system composed of two condensing components ($H_2O$ and $H_2SO_4$) is produced in the gases. The behavior of this system with varying temperature is characterized by a diagram (Fig. 102) constructed in the coordinates t, $\%SO_3$ for a particular value of the vapor-mixture

pressure.

The upper curve (dew point) separates the superheated-steam region from the wet-steam region, while the lower curve (boiling line) separates [the latter] from the liquid region. Point a corresponds to an $SO_3$ content of 0, i.e., to pure water vapor, while point b corresponds to 100% $H_2SO_4$. In other words, a is the dew point of water vapor, and b is the dew point of 100% $H_2SO_4$. It may be seen that even insignificant contents of $SO_3$ in the vapors produce sharp increases in dew point as compared with that of pure water vapor, and that the condensate deposited when this happens is sulfuric acid of one concentration or another [28].

M.S. Smirnov used the device [19, 28] whose diagram is shown in Fig. 103 to determine the dew point of the combustion products of sulfur-containing fuels in diesels. The device consists of a row of parallel, sequentially connected tubes made from tinplate and installed in a tank with coolant water. The exhaust gases from the engine's exhaust manifold enter the first tube on the left and, passing through all of the tubes, are released into the atmosphere. The temperature of the combustion products is measured simultaneously by six thermometers.

When heat is withdrawn from a gas that is not saturated with water vapor, its temperature will drop approximately linearly with diminishing heat content. When the gas temperature reaches the dew point, moisture begins to precipitate and the latent heat of condensation is released. This will be expressed by a break in the cooling curve that will characterize the dew point.

Figure 104 presents the cooling curves obtained by M.S. Smirnov for the combustion products of fuels with various sulfur contents as produced by a 3D-6 engine, which operated in all cases at full power. For fuels containing 0.9, 1.0 and 1.25% sulfur, the dew point lies in

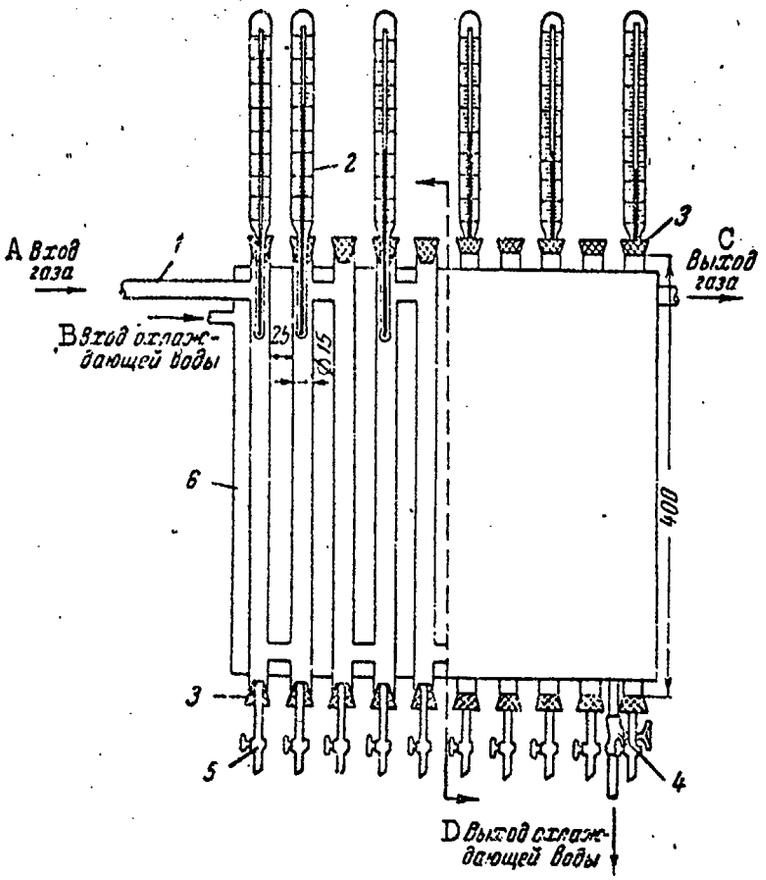


Fig. 103. Diagram of apparatus for determining dew point of combustion products in diesels. 1) Tube for introduction of combustion products; 2) thermometers; 3) rubber stoppers; 4) valve for drainage of coolant water; 5) glass stopcocks for drainage of condensate; 6) coolant-water tank. A) Gas inlet; B) coolant-water inlet; C) gas outlet; D) coolant-water outlet.

the range from 110 to 130°. For a fuel containing 0.18% sulfur, the dew point is 58°. Consequently, all other fuel-combustion conditions the same, a consistent dependence of dew point on fuel sulfur content is established.

Measurements made by the same author indicated that in all operating modes of the 3D-6 engine, the cylinder-sleeve temperature is 100 to 110° at the top and bottom and 60 to 95° in the middle part, which is most effectively cooled, i.e., given these relationships between the temperatures of the cylinder liners and the dew points of sulfur-fuel combustion products, formation of sulfuric acid is inevitable ...

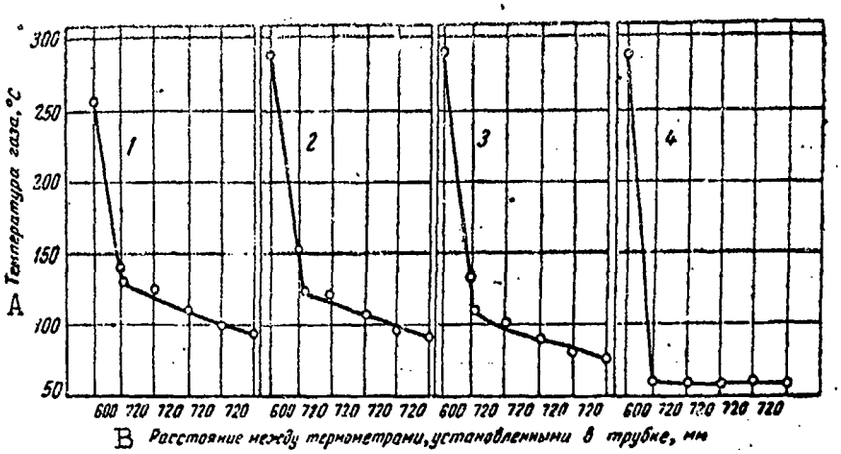


Fig. 104. Dew point for fuel products of combustion. 1) Sulfur fuel (1.25% sulfur); 2) sulfur fuel (1% sulfur); 3) sulfur fuel (0.9% sulfur); 4) low-sulfur fuel DS, GOST 4749-49 (0.18% sulfur). A) Gas temperature, °C; B) distance between thermometers in tube, mm.

only in the crankcase, but also on the working parts of the cylinder liners.

The influence of the air excess and the residence time of the mixture in the high-temperature zone on the dew point is extremely strong. Figure 105 presents the results of dew-point measurements made for a number of fuels with various sulfur contents and air:fuel ratios, as obtained in a miniature combustion chamber – a model of a gas-turbine combustion chamber [29]. The dew point and, consequently, the sulfuric-anhydride content in the combustion products increase sharply as the sulfur content in the fuel increases from zero to 1%; as the sulfur content rises from 1 to 4%, the dew point continues to rise, but does so somewhat more slowly. The dew-point depression with increasing excess of air is produced precisely by the drop in the $SO_3$ concentration in the combustion products. Although the rise in the oxygen partial pressure contributes to formation of $SO_3$, the increased speed of the gas resulting from its increased volume and the shortened residence time of each gas molecule in the high-temperature zone offsets the effects of the first factor.

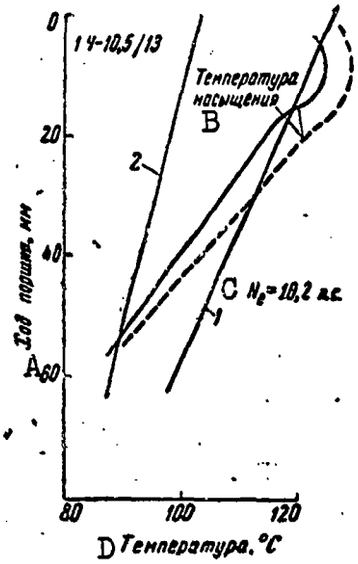


Fig. 106. Change in saturation temperature of water vapor over piston stroke in 1Ch-10.5/13 diesel. 1) Temperature along generatrix of cylinder at 1500 rpm; 2) temperature along cylinder generatrix at 900 rpm. A) Piston stroke, mm; B) saturation temperature; C) $N_e$ = 10.2 hp; D) temperature, °C.

was found to be below 100°. As a rule, the problem of low-temperature corrosion is unimportant for these engines because of the high gas temperature in the exhaust, although further utilization of the lost heat, as in utilizer boilers, may create conditions for the appearance of low-temperature corrosion.

## CORROSION OF RECIPROCATING INTERNAL-COMBUSTION ENGINE COMPONENTS

The presence of sulfur and its compounds in fuels used in reciprocating internal-combustion engines may cause low-temperature and high-temperature corrosion.

The possibility of condensation of water or sulfuric-acid vapor on the surfaces of the engine components depends on the temperature of these components and external conditions: the moisture content of the gaseous combustion products, their $SO_3$ content, the temperature and the pressure. For the cylinder-and-piston group of the engine, which is the basic target of low-temperature corrosion by sulfur-fuel combustion products, these conditions change continuously together with changes in combustion-chamber volume and the state of the gases as a result of the reciprocating motion of the piston. The experimental results obtained by L.V. Malyavinskiy and I.A. Chernov [26] in a 1Ch-10.5/13 diesel, which are shown in Fig. 106, may serve as an illustration; they show the change in the saturation temperature of the water vapors over the engine's piston stroke with (solid lines) and without (broken lines) consideration of the vapor content of the air.

At 900 rpm, the condensation of moisture from the combustion products is possible over the entire height of the cylinder sleeve, while at 1500 rpm, it may occur at its top. Figure 107, a and b, gives analogous curves for the GAZ-51 and M-103 carburetor engines.

Irrespective of the presence of sulfur-combustion products in the gases, the presence of water vapor and carbon dioxide and their condensation on the engine's cylinder walls may produce a corrosion process. A sharp increase in piston-ring and cylinder-sleeve wear with diminishing temperature of the latter was distinctly demonstrated by the experiments of Williams [32], as well as in the tests conducted by Kendall and Greenshields [33].

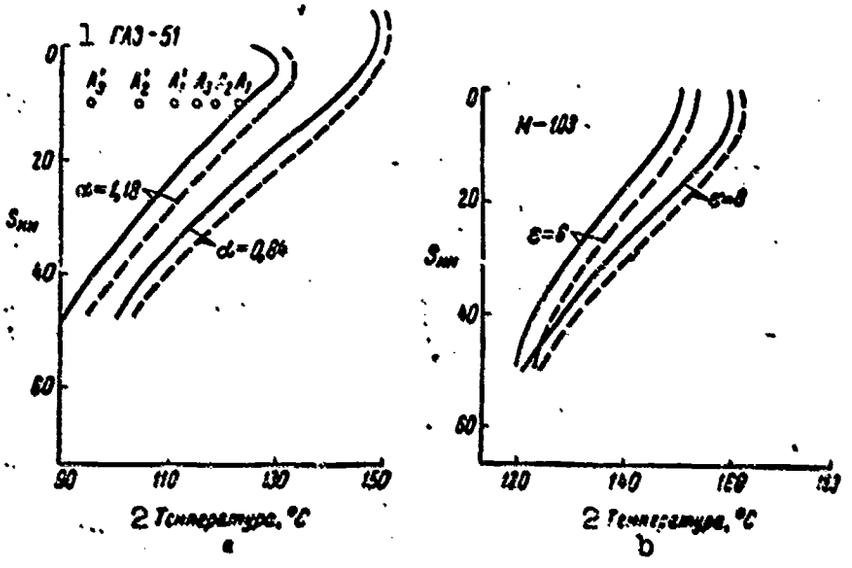


Fig. 107. Variation of saturation temperature of water vapor over piston stroke in engines. a) GAZ-51 engine; b) M-103 engine. $A_1$, $A_2$, $A_3$) Wall temperatures of cylinders 4, 5 and 6 at 2100 rpm: $A'_1$, $A'_2$, $A'_3$) same at 700 rpm. 1) GAZ-51; 2) temperature, °C.

When $SO_3$ is present in the combustion products, the saturation temperature is shifted into a region of even higher values, so that condensation of sulfuric acid on the cylinder-sleeve walls is made easier.

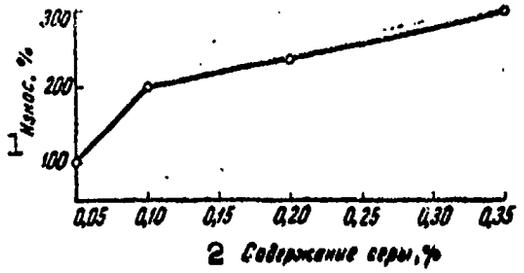


Fig. 108. Influence of sulfur content in gasoline on cylinder-sleeve wear. 1) Wear, %; 2) sulfur content, %.

As a result of the thermal dynamic and design peculiarities of the various reciprocating engines, sulfur in the fuel produces more rapid corrosion and wear of parts in the cylinder-piston group of carburetor engines than in diesels, in water-cooled engines than in air-cooled engines, and in stressed engines with high compression ratios than in less highly stressed engines. Greater corrosive wear is also characteristic for engines operating at low speeds, with frequent starting and sharp transitions from part load to full load.

In stationary low-speed engines with thick and consequently hot cylinder-sleeve walls used in steady operating modes, cylinder corrosion and wear are moderate even in operation on fuels with very high sulfur contents (up to 3.0-3.5%).

Investigating the influence of sulfur content in gasoline on the wear of cylinder sleeves and piston rings in a single-cylinder engine with a bore and stroke of 85 mm, Williams [34] found that an increase in sulfur content from 0.01 to 0.08% approximately doubles the rate of wear.

Cattaneo and Starkman [35], who studied the influence of sulfur at contents from zero to 0.4% in the gasoline on wear in a Chevrolet engine at a cooling temperature of 35°, established a linear relationship for wear as a function of sulfur content. According to these au-

thors, wear approximately doubles when the sulfur content rises from zero to 0.1%.

Figure 108 shows the influence of increasing sulfur content in the gasoline (from 0.05 to 0.35%) on wear of an engine's cylinder sleeves in 220-hour tests (acccrding to N.S. Semenov [36]). An increase in sulfur content from 0.05 to 0.10% doubles the rate of wear. It was shown by the same tests that the increase in the clearance at the compression-ring joint reaches 250-400%.

Many investigators [19, 24, 37-41] have studied the influence of sulfur in the fuel on wear in diesels. The results of their investigations are summarized in a series of monographs that have been published in recent years [19, 35, 38-40]. The consensus is that as the sulfur content in a diesel fuel rises from 0.2% (fuel from Baku petroleums) to 1.0-1.2% (fuels from petroleums of Far Eastern fields), wear of the diesel's cylinder-and-piston group increases by a factor of 2-6. The factor by which wear is accelerated depends on the type of engine and the conditions under which it is operating.

The results of tests of a series of domestic automotive and tractor engines on fuels with various sulfur contents (Table 55) as summarized by N.G. Puchkov [39] may be used to illustrate the above. The tractor engines (KDM-46 and D-54), which have small ratios of cylinder working surface to cylinder volume, are less sensitive to attack by products of sulfur combustion than the highly stressed YaAZ-204 automotive engine.

Table 56 presents data of M.S. Smirnov [19] that characterize the wear of the principal parts of a 1Ch-10.5/13 engine after 500 hours of operation on fuels with various sulfur contents.

All of the above applies to high-speed highly stressed diesels. The low-speed heavy-duty marine and stationary diesels operate dep-

TABLE 55

Wear of Cylinder Sleeves with Various Sulfur Contents in Fuel

| 1 Двигатель | 2 Длительность испытаний | 3 Износ цилиндров (в мк) при содержании серы в топливе, % | | | |
|---|---|---|---|---|---|
| | | 0,2 | 0,6 | 1,0 | 1,3 |
| | | 4 Стендовые испытания | | | |
| 5 ЯАЗ-204 | 550 час. 9 | 100 | 115 | 140 | — |
| 6 Д-35 | 1000 » | 39 | — | 70 | — |
| 7 Д-54 | 1000 » | 30 | 64 | — | — |
| 8 КДМ-46 | 1000 » | 48 | — | 52 | — |
| | | 11 Эксплуатационные испытания | | | |
| 5 ЯАЗ-204 | 1000 км 10 | 5,6 | 4,5 | 8,6 | — |
| 5 ЯАЗ-204 | 1000 » | 3,0 | 6,5 | — | 16,2 |
| 6 Д-35 | 1000 час. 9 | 230 | 280 | 440 | — |
| 7 Д-54 | 1000 » | 100 | 120 | 150 | — |
| 8 КДМ-46 | 1000 » | 50 | 70 | 90 | — |

1) Engine; 2) duration of tests; 3) cylinder wear (in μ) for sulfur content in fuel of [%]; 4) bench tests; 5) YaAZ-204; 6) D-35; 7) D-54; 8) KDM-46; 9) hours; 10) km; 11) operational tests.

ably on fuels with sulfur contents up to and above 3%. Steinitz [42] explains this in terms of the great thickness of the cylinder walls and the presence of a special lubrication system in which the oil is fed directly onto the cylinder wall. This accounts for the long service lives of the engines – up to 15,000 hours without overhaul for a total time as long as 20 years.

It might be thought that the increase in engine wear observed with the use of high-sulfur fuels results not simply from the corrosive action of the combustion products. Intensified scaling and varnish formation on the hot components of the engine are generally observed when this happens: this contributes to burning-on or at least reduced mobility of the piston rings. As a rule, the scale that forms is harder than that formed in operation on low-sulfur fuels, and this may also be a cause of accelerated wear.

TABLE 56

Wear on Principal Components of 1Ch-10.5/13 Engine after 500 Hours of Operation

| 1 Деталь | 2 Износ (в мм) при работе на топливе с содержанием серы, % | |
|---|---|---|
| | 0,18 | 0,90 |
| 3 Гильза цилиндра | 0,02 | 0,08 |
| 4 Поршень | 0,01 | 0,04 |
| 5 Вкладыши шатуна | 0,02 | 0,06 |
| 6 Верхняя втулка шатуна | 0,05 | 0,07 |
| 7 Шатунная шейка колепчатого вала | 0,005 | 0,013 |
| 8 *Компрессионные кольца* | | |
| 9 Увеличение зазора в стыке | 0,30 | 1,23 |
| 10 Потеря в весе | 0,26 (г) | 0,79 (г) |
| 11 *Маслосбрасывающие кольца* | | |
| 12 Увеличение зазора в стыке | 0,25 | 0,53 |
| 13 Потеря в весе | 0,11 (г) | 0,22 (г) |
| | 14 | |

1) Component; 2) wear (in mm) during operation on fuel with sulfur content of [%]; 3) cylinder sleeve; 4) piston; 5) connecting-rod bearing insert; 6) top-end bushing; 7) crankshaft journal; 8) compression rings; 9) increase of gap at joint; 10) weight loss; 11) oil-control rings; 12) increase in gap at joint; 13) weight loss; 14) grams.

Nevertheless, corrosive wear is of fundamental importance, as indicated by the influence of coolant-water temperature on wear rate that has been observed by all investigators. The data of B.B. Genbom [37], which are given in Fig. 109, may serve as an example. Wear doubles as the coolant temperature is lowered from 90° to 30°. For a fuel containing 0.7% sulfur, Moore and Kent [33] showed that a change in coolant-water temperature from 71° to 38° results in a 3- to 4-fold increase in the rate of piston-ring wear. Consequently, the role taken by low-temperature corrosion in accelerating wear of the engine's cylinder-and-piston group in operation on high-sulfur fuel may be reg-

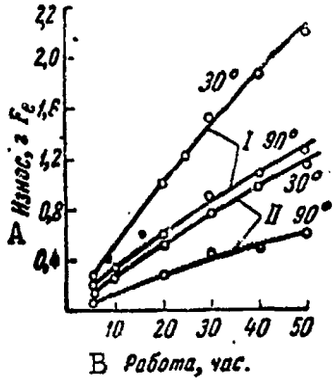


Fig. 109. Influence of coolant-water temperature on rate of wear. I) Sulfur content in fuel 0.995%; II) sulfur content in fuel 0.127%. A) Wear, g of Fe; B) hours of operation.

as established beyond question.

For internal-combustion engines operating on high-sulfur fuels, it appears that high-temperature corrosion is not of grave importance. Isolated cases of exhaust-valve corrosion have been observed in operation of diesels; however, this corrosion never assumed catastrophic dimensions. It is characteristic that, in analyzing typical causes of valve failure and malfunction in his monograph, K. Georgi [33] makes no mention at all of high-temperature corrosion of the valves by combustion products of sulfur fuels.

The following observation is also of interest [43]: long-term comparative tests of two gasolines with sulfur contents of 0.06-0.14% and 0.25-0.30% were run on 62 motor vehicles of various types operating under different loads and under a variety of climatic and road conditions. The following results were established.

1. The high-sulfur gasoline had no detrimental effect on the operation and service life of the valves.

2. Muffler service life and exhaust-system corrosion were the same for operation on either gasoline.

3. Piston-ring and cylinder-sleeve wear in operation on the high-sulfur gasoline under low-load conditions with frequent starting was 2-5 times that observed in operation on the fuel containing less sulfur. Wear was the same in operation under heavy loads on long runs.

Somewhat different conclusions were arrived at by K.S. Ramayya, who showed that at the temperatures prevailing on the friction surfaces of the engine's cylinder-and-piston group (100-150°), gaseous

sulfuric anhydride may be a direct cause of corrosion and increased wear [44]. However, the results of these experiments, which were performed on a laboratory simulation apparatus [45], can hardly be transferred directly to an engine and, moreover, the possibility is not excluded that oxidation of $SO_2$ to $SO_3$ took place under the conditions of the experiment.

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[List of Transliterated Symbols]

346 кр = kr = kriticheskiy = critical

346 опт = opt = optimal'nyy = optimum

## Chapter 13

## COMPOSITION AND PROPERTIES OF BASE FUELS AND COMPONENTS

Commercial grades of various fuels, as a rule, are mixtures of two, three, or more component parts. That particular component which makes up the greatest portion of the fuel composition is referred to as the base fuel.

To improve the physicochemical and operational properties of the base fuels, a whole number of substances are added to these fuels, and these substances can be divided into three basic groups, depending on the nature of the reaction and the quantity added: components, additives, and antiknock additives (see Chapters 13 and 14).

Components are added to base fuels in quantities ranging from 5 to 40%; additives are added in quantities of 2 – 5% to improve antiknock properties; to raise the cetane numbers, additives are added in quantities ranging from 0.5 – 3%; in order to improve the operational properties of a fuel, additives are added in quantities ranging from 0.004 to 1 – 2%. The quantity of antiknock additive added to a fuel does not exceed 0.2 – 0.3%.

### BASE FUELS

Products of various petroleum-refining processes are employed as base fuels, and we have reference here to such processes as direct distillation, thermal and catalytic cracking, catalytic reforming, hydrogenation of coal tar and heavy petroleum residues, synthesis from carbon monoxide and hydrogen (water gas), and the processing of shales.

The above-enumerated products differ markedly from one another in terms of their physicochemical and operational properties. It should be borne in mind that one and the same product may be used to obtain certain fuels which are to serve as base fuels, whereas others are to be used as fuel components. Below we present a discussion of the properties of all the products from the basic processes in the refining of petroleum and other raw materials, regardless of whether or not these products are used exclusively as base fuels or whether employed primarily as a fuel component.

Products of the Direct Distillation of Petroleum

The following products from the direct distillation of petroleum serve as base fuels: gasolines, ligroins, kerosenes, gas oils, and solar distillates.

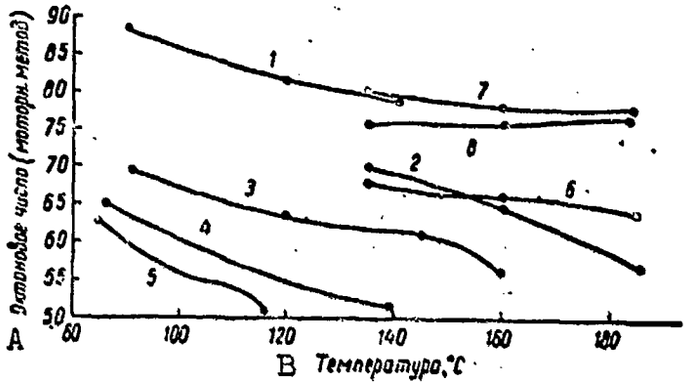


Fig. 110. Effect of end of boiling or 90% distilled temperatures on the octane number of these gasolines [1]. 1) Gasoline from heavy Malgobek petroleum; 2) direct-distillation gasoline (90% distilled); 3) gasoline from Groznyy paraffinic petroleum; 4) gasoline from Tuymazy petroleum; 5) synthol; 6) thermal-cracking gasoline (90% distilled); 7) catalytic-cracking gasoline (90% distilled); 8) catalytic-reforming gasoline (90% distilled); A) Octane number (motor method); B) temperature, °C.

Direct-distillation gasolines are used for aviation and automotive gasolines; ligroins are used for fuels in carburetor tractors;

kerosenes are used primarily for jet and diesel fuels; gas oils and solar distillates are used primarily for diesel fuels. Direct-distillation products such as heavy ligroin or a wide fraction boiling over within a range of from 60 to 280° may be used as fuels for turbocompressor air-reaction engines.

The majority of the direct-distillation gasolines consist primarily (90 – 95%) of paraffinic and naphthenic hydrocarbons. The aromatic-hydrocarbon content does not exceed 5 – 9%; the gasolines from the Verkhne-Chusovskiye Gorodki petroleums, containing from 30 to 50% aromatic hydrocarbons are an exception, as are the gasolines from the Maykop petroleum which contains up to 13% aromatic hydrocarbons. There are no unsaturated hydrocarbons in direct-distillation gasolines.

Direct-distillation gasolines exhibit high stability, are not subject to resinification during storage, and they have a low freezing point (below -100°). Direct-distillation gasolines obtained from the various petroleums of the Soviet Union differ markedly between one another both in terms of chemical composition and in terms of antiknock properties.

As a rule, gasolines containing from 55 to 70% paraffinic hydrocarbons have an octane number, in pure form, of 50 – 65 units, and with 3 – 4 ml/kg ethyl fluid, 83 – 87 units. Gasolines containing 50 – 70% naphthenic hydrocarbons have octane numbers, in pure form, of 70 – 73, and with 3 – 4 ml/kg ethyl fluid, 90 – 95 units.

An exception are the aviation gasolines containing large quantities of isoparaffinic hydrocarbons with two branched methyl groups. For example, gasolines from Voznesensk petroleum, as well as gasolines from Sagiz and from heavy Malgobek petroleum, containing up to 60 – 65% isoparaffinic hydrocarbons, exhibit octane numbers, in pure form, of 75 – 30, and with 3 – 4 ml/kg ethyl fluid, 90 – 97 units.

Direct-distillation gasoline grades vary within a very wide range: gasolines rich in naphthenes are graded higher than gasolines rich in paraffinic hydrocarbons.

The antiknock properties of direct-distillation gasolines are strong functions of the fractional composition of these gasolines. As a rule, as the boiling range of the direct-distillation gasolines increases, the antiknock properties of these gasolines experience pronounced impairment (Fig. 110).

High requirements are imposed on the antiknock properties of aviation gasolines. As the fractional composition becomes heavier, the antiknock properties of direct-distillation gasolines are impaired, so that the boiling range of these gasolines is strictly limited in the production of aviation gasolines not only with respect to the uppermost permissible boiling limit of 97.5% of the fuel (180°), but in terms of the antiknock properties of the gasoline in question. The poorer the antiknock properties of gasolines contained in some petroleum, the lower the temperature required in order to restrict the boiling off of 97.5%. As a result, the boiling point of 50, 90, and 97.5% direct-distillation gasolines varies over a wide range. For example, the 97.5% temperature for various gasolines lies in a range from 115 - 170°, and for a 90% gasoline, the temperature ranges from 106 to 145°.

The temperature that corresponds to the beginning of boiling and to the boiling over of 10% of direct-distillation gasolines used to produce aviation gasolines also varies within a rather wide range of temperatures (start of boiling 42 - 86°; 10% distilled, 65 -92°). In this case, the direct-distillation gasolines, rich in naphthenes (the majority of the Baku and Sakhalin gasolines), exhibit high temperatures for the start of boiling and for the boiling over of 10% and, conversely, the gasolines rich in paraffinic hydrocarbons (Groznyy,

Krasnodar, and the gasolines from the Ural-Volga deposits) exhibit low temperatures for the start of boiling and for the boiling over of 10%.

In terms of antiknock properties and fractional composition, not all of the gasolines can be employed as base fuels for the production of aviation gasolines. In this regard, the potentials of automotive fuels are substantially greater.

Higher-boiling direct-distillation products (kerosenes, gas oils, solar distillates), obtained from the various petroleums of the Soviet Union, differ even more markedly with respect to chemical composition than do gasolines. In addition to the monocyclic hydrocarbons, the kerosene fractions may contain substantial quantities of bicyclic naphthenic and aromatic hydrocarbons, and in the higher-boiling fractions, components of diesel fuel, tricyclic compounds are possible.

TABLE 57

Solidification Temperature and Cetane Number of Diesel Fuels Having Various Hydrocarbon Group Compositions

| 1 Образцы дизельного топлива | 2 Групповой углеводородный состав | | | Температура застывания, 6 °С | 7 Цетановое число |
|---|---|---|---|---|---|
| | 3 парафино-нафтеновые углеводороды | 4 парафиновые углеводороды и боковые цепи | 5 ароматические углеводороды | | |
| № 1 | 72,0 | 56,5 | 28,0 | —26 | 39 |
| № 2 | 78,3 | 44,5 | 21,7 | —60 | 40 |
| № 3 | 75,2 | 64,8 | 24,8 | —35 | 43 |
| № 4 | 78,4 | 57,7 | 21,6 | —11 | 56,4 |
| № 5 | 76,4 | 67,6 | 23,6 | —12 | 60 |

1) Specimens of diesel fuel; 2) hydrocarbon group composition; 3) paraffinic-naphthenic hydrocarbons; 4) paraffinic hydrocarbons and side chains; 5) aromatic hydrocarbons; 6) solidification temperature, °C; 7) cetane number.

Because of the great difference in the chemical composition of the kerosenes derived from the various petroleums, the octane numbers of these kerosenes vary within a very wide range: from zero and be-

low for kerosenes derived from Groznyy paraffinic and certain other petroleums, to 50 – 55 for kerosenes derived from a number of Emba, Far Eastern, and some Groznyy petroleums. As a rule, the octane numbers of the kerosenes increase as the aromatic-hydrocarbon content rises, but when there is a high paraffinic-hydrocarbon content in conjunction with a high aromatic-hydrocarbon content (particularly in the case of normal structure or little branching for the former), the kerosene octane number is relatively low. The kerosene octane number is a function of the nature of the aromatic and particularly of the naphthenic hydrocarbons. Bicyclic naphthenic hydrocarbons have higher octane numbers than the monocyclic hydrocarbons that correspond to the bicyclic naphthenic hydrocarbons in terms of molecular weight.

The diesel-fuel cetane number drops with an increase in the aromatic-hydrocarbon content, and this pertains especially to the bicyclic hydrocarbons. Conversely, with an increase in normal-structure and little-branched paraffinic hydrocarbons in the diesel fuel, the cetane number of the diesel fuel increases; there is a simultaneous rise in the solidification temperature of the fuels. Fuels rich in monocyclic naphthenic hydrocarbons and, to a lesser extent, in bicyclic hydrocarbons, exhibit low solidification temperatures and more or less acceptable cetane numbers.

Table 57 shows the limits of change for the cetane numbers and solidification temperatures of diesel fuels derived from petroleums having various hydrocarbon group compositions.

The group hydrocarbon composition of the products obtained from the direct distillation of even a single petroleum is not constant. As the boiling point of the direct-distillation product rises, the content of certain classes of hydrocarbons increases, whereas the content of other hydrocarbon classes decreases. The hydrocarbon composi-

tion of petroleums from various deposits changes in various ways. The content of aromatic hydrocarbons increases as the boil-off temperature limits for the direct-distillation product increase, and this all the more so, the lower their content in the initial product. The greatest increase in the content of aromatic hydrocarbons (on the average from 4 – 9% to 12 – 27%) takes place within a temperature range from 170 to 230°. In higher-boiling products, the aromatic-hydrocarbon content is either stabilized or experiences an insignificant increase.

The content of naphthenic hydrocarbons in direct-distillation products increases with a rise in the boiling point, whereas the content of paraffinic hydrocarbons drops; however, in certain products rich in naphthenic hydrocarbons (Surakhany select and Kara-Chukhur petroleums), vice versa, the content of naphthenic hydrocarbons diminishes, whereas the paraffinic hydrocarbon content increases. In a number of high-paraffinic direct-distillation products (petroleums from Ural-Volga deposits, Groznyy paraffinic, etc.), containing more than 60 – 70% paraffinic hydrocarbons in the low-boiling fractions (up to 100 – 120°), the content of paraffinic hydrocarbons diminishes with a rise in the boil-off temperature (within a range below 300°) only to 50 – 60%, or there may be absolutely no reduction in the content of the paraffinic hydrocarbons. Therefore, the direct-distillation products of such petroleums cannot be used at all as tractor kerosene. In the derivation of jet fuels which use these products as a base, the upper boil-off limit must be severely restricted in order to provide for a solidification temperature that does not exceed -60°. A high solidification temperature makes it possible to make only summer and special grades of diesel fuels from these products. This same restriction must be observed for direct-distillation products obtained from petroleums of the Surakhany select type. Products containing a large

quantity of aromatic hydrocarbons, because of a low cetane number, cannot be used for the production of diesel fuels, nor can they be used for jet-engine fuels in which the aromatic-hydrocarbon content is restricted.

Figure 111 shows the group hydrocarbon composition of narrow kerosene-gas-oil fractions of Tuymazy petroleum.

In the direct-distillation products of almost all petroleums we find sulfur compounds. The quantity of these compounds is insignificant in a number of petroleums. In the products obtained from petroleums from the Ural-Volga deposits, as well as in products from certain Central Asian petroleums (Uch-Kizilskiy and Khaudag), there is a significant quantity of sulfur compounds. The quantity of these compounds increases as the boiling-point limits of these products rise (Fig. 112).

Table 58 shows the distribution of sulfur in the sulfur compounds contained in commercial diesel fuels.

We can see from the data in the table that with an increase in the total sulfur content in the fuel, there is an increase in the content of sulfides and residual sulfur compounds which generally include thiophenes in their composition. The sulfides and residual sulfur compounds total more than 90% (up to 98 - 99%) of all the sulfur compounds contained in diesel fuels. The content of disulfides and mercaptans does not depend on the total quantity of sulfur in the diesel fuel.

Since the content of sulfur is rigorously restricted in all fuels, direct-distillation products derived from high-sulfur petroleums cannot under any circumstances be used for the production of aviation gasolines, nor for jet and diesel fuels. For products derived from petroleums containing smaller quantities of sulfur, the upper boiling limit must be restricted.

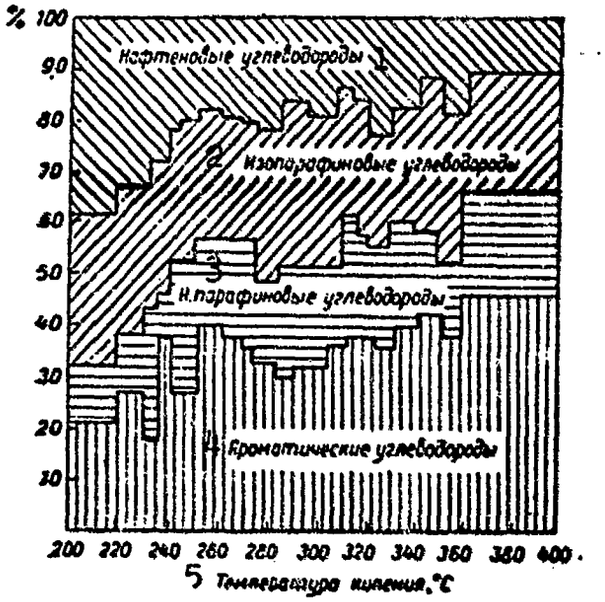


Fig. 111. Group hydrocarbon composition of narrow kerosene-gas-oil fractions of Tuymazy petroleum [2]. 1) Naphthenic hydrocarbons; 2) isoparaffinic hydrocarbons; 3) naphthenic-paraffinic hydrocarbons; 4) aromatic hydrocarbons; 5) boiling point, °C.

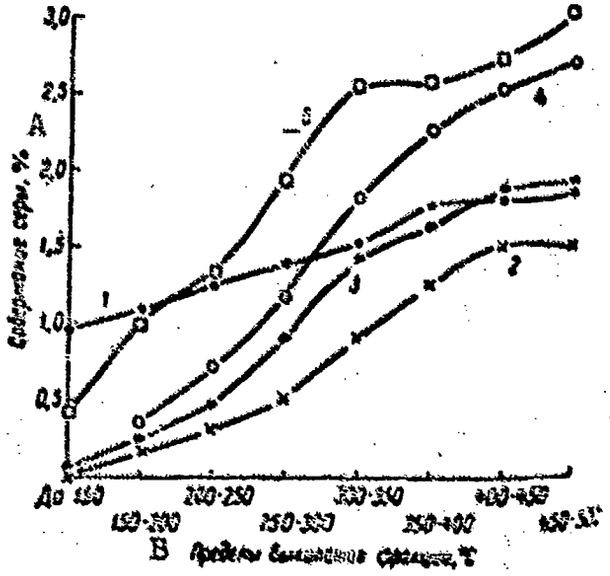


Fig. 112. Distribution of sulfur compounds in petroleum products, depending on the boiling range of these products [3]. 1) Petroleum from the Mukhanovo deposit (Kungur stratum); 2) the same, (carboniferous stratum); 3) petroleum from the Zol'noye ravine deposit (carboniferous stratum); 4) petroleum from the Yablonovo ravine deposit (carboniferous stratum); 5) petroleum from the Krasnoyarka deposit (Arti stratum). A) Sulfur content, %; B) boiling limits of fractions, °C.

TABLE 58

Group Composition of Sulfur Compounds in Diesel Fuels [4]

| 1 Плотность $\rho_4^{20}$ | 2 Фракционный состав | | | | | 5 Содержание серы, % | 3 Состав сернистых соединений, % на серу | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4 н. к. | 10% | 50% | 90% | 96% | | 6 элементарная сера и сероводород | 7 меркаптаны | 8 сульфиды | 9 дисульфиды | 10 остаточная сера |
| 0,795 | 154 | 175 | 202 | 246 | 321 | 0,3 | 11 Отсутствуют | 0,0129 | 0,230 | 0,016 | 0,04 |
| 0,815 | 145 | 181 | 229 | 287 | 321 | 0,64 | То же | 0,0323 | 0,275 | 0,01 | 0,32 |
| 0,838 | 198 | 227 | 268 | 328 | 360 | 0,74 | 12 » | 0,0148 | 0,360 | 0,014 | 0,35 |
| 0,842 | 205 | 240 | 273 | 327 | 348 | 1,0 | » | 0,0078 | 0,360 | 0,008 | 0,62 |
| 0,847 | 175 | 238 | 282 | 359 | — | 1,1 | » | 0,0305 | 0,50 | 0,01 | 0,55 |
| 0,837 | 185 | 230 | 280 | 343 | 350 | 1,16 | » | Отсутствуют | 0,45 | 0,016 | 0,69 |

1) Density, $\rho_4^{20}$; 2) fractional composition; 3) composition of sulfur compounds, in % of sulfur; 4) start of boiling; 5) content of sulfur, %; 6) elementary sulfur and hydrogen sulfide; 7) mercaptans; 8) sulfides; 9) disulfides; 10) residual sulfur; 11) none; 12) the same.

Thermal-Cracking Products

From among the thermal-cracking products gasolines are used as base fuels for the production of automotive gasolines and kerosenes are used for the production of tractor fuels and as components in diesel fuels as well as components in fuels for jet engines. The hydrocarbon composition of the thermal-cracking products is determined by the conditions of the process and the nature of the initial raw material (crude). The basic feature that these products have in common is the presence of substantial quantities of unsaturated hydrocarbons.

As the fractional composition of the thermal-cracking products becomes heavier, the presence (content) of unsaturated hydrocarbons in these products, as well as the presence (content) of paraffinic hydrocarbons, diminishes (Table 59). Conversely, the content of naphthenic and aromatic hydrocarbons increases.

TABLE 59

Group Hydrocarbon Composition of Thermal-Cracking Products

| 1 Пределы выкипания фракций, °С | 2 Непасыщенные углеводороды | 3 Парафиновые углеводороды | 4 Нафтеновые углеводороды | 5 Ароматические углеводороды |
|---|---|---|---|---|
| 45—215 | 35,8 | 50,6 | 7,4 | 6,2 |
| 136—229 | 25,6 | 40,8 | 27,1 | 6,5 |
| 120—290 | 25,7 | 33,9 | 26,3 | 14,7 |
| 211—265 | 17,1 | 34,9 | 27,4 | 20,6 |
| 252—303 | 17,0 | 21,9 | 30,0 | 31,1 |

1) Boiling limits for fractions, °C; 2) unsaturated hydrocarbons; 3) paraffinic hydrocarbons; 4) naphthenic hydrocarbons; 5) aromatic hydrocarbons.

TABLE 60

Composition of Unsaturated Hydrocarbons in a Thermal-Cracking Distillate [6]

| 1 Непасыщенные углеводороды | 2 Температуры выкипания фракции, °С | | | | | |
|---|---|---|---|---|---|---|
| | 60—95 | 95—122 | 122—150 | 150—175 | 175—200 | > 200 |
| 3 Суммарное содержание . . | 45,0 | 37,0 | 34,8 | 31,7 | 26,5 | 20,5 |
| 4 В том числе: | | | | | | |
| 5 диолефины . . . . . | 2,4 | 2,3 | 1,9 | 1,5 | 1,1 | 1,0 |
| 6 олефины . . . . . | 35,1 | 28,1 | 20,9 | 6,8 | 3,3 | 4,9 |
| 7 циклоолефины . . . . | 6,9 | 8,6 | 8,5 | 18,7 | 14,9 | 6,5 |
| 8 ароматические углеводороды с двойной связью в боковой цепи . . . . . | 0 | 0 | 3,3 | 4,7 | 7,2 | 7,3 |

1) Unsaturated hydrocarbons; 2) boiling point of fractions, °C; 3) total content; 4) including; 5) diolefins; 6) olefins; 7) cycloolefins; 8) aromatic hydrocarbons with double bond in side chain.

There are olefins, cycloolefins, aromatic hydrocarbons with a double bond in the side chain, as well as small quantities of diolefins and cyclodiolefins (Table 60) in thermal-cracking products. The latter are generally found in the head fractions of gasoline. In thermal-cracking gasolines of lightened fractional composition, the unsaturated hydrocarbons are represented primarily by the olefins and the cycloolefins.

The olefins are concentrated in the low-boiling products. The con-

TABLE 61

Nature of Unsaturated Hydrocarbons in Thermal-Cracking Products of Various Fractional Compositions [5]

| 1 Пределы выкипания фракций, °С | 2 Содержание, считая на ненасыщенные углеводороды, % | | |
|---|---|---|---|
| | 3 олефины | 4 циклоолефины | 5 ароматические с двойной связью в боковой цепи |
| 45—215 | 33 | 37 | 30 |
| 136—229 | 9 | 18 | 73 |
| 211—265 | 3,5 | 7,0 | 89,5 |
| 252—303 | 0 | 14 | 86 |

1) Boiling limits of fractions, °C; 2) content, referred to the unsaturated hydrocarbons, %; 3) olefins; 4) cycloolefins; 5) aromatic hydrocarbons with double bond in side chain.

tent of cycloolefins initially increases as the fractional composition of the product becomes heavier, and subsequently the content is reduced, attaining its maximum in the 150 – 175° fraction. Beginning with the 122 – 150° fraction, aromatic hydrocarbons with a double bond in the side chain appear in the thermal-cracking products. As the boiling limit temperature increases, the quantity of these aromatic hydrocarbons (with the double bond in the side chain) increases, and they make up the dominant mass of the unsaturated hydrocarbons in the high-boiling products (Table 61).

Unsaturated compounds are outstanding because of their low stability. Under the action of light, temperature, the oxygen of the air, and the catalytic action of metals, these compounds are subject to rapid oxidation and polymerization. As a result of these processes, resinous substances are formed and are accumulated in the thermal-cracking products, as are acids and similar undesirable substances.

The investigations that have been carried out on the experimental storage of gasolines containing unsaturated compounds of various structures have shown that the olefins exhibit little tendency to tar for-

mation, while the diolefins and aromatic hydrocarbons with an unsaturated bond in the side chain form tars within a short period; in this case, the diolefins form tars, given any (even the most insignificant) concentrations in the gasoline. In the presence of diolefins, even the olefins begin to undergo oxidation leading to the formation of tars.

Depending on the predominant content of certain unsaturated hydrocarbons in the various thermal-cracking products, these may differ markedly between one another in terms of stability.

To increase the stability of the cracking products, i.e., to prevent the resinification of the cracking products, special substances are employed, and these are referred to as antioxidants (see Chapter 14).

In view of the high content of unsaturated hydrocarbons in the thermal-cracking products, the octane numbers of these products are somewhat higher than the octane numbers of corresponding direct-distillation products derived from the same petroleum. However, as a rule, the absolute values of the octane numbers of thermal-cracking gasolines are relatively low and, depending on the initial crude, vary within a range of 58 – 68 units during the cracking process and procedures. The octane numbers of gasolines produced by the thermal-cracking method are, to a lesser extent than direct-distillation gasolines, functions of the end-of-boiling point of the thermal-cracking gasolines (see Fig. 110).

Catalytic-Cracking Products

Catalytic-cracking gasolines and gas oils are used for the production of fuels; the gasolines are used as the base fuels for the production of aviation gasolines, and the gas oils are used primarily as components for the production of diesel fuels and fuels for carburetor tractor engines. In addition, catalytic-cracking gasoline (as a

TABLE 62

Characteristic of Catalytic-Cracking Gasolines

| 1 Назначение | 6 Плотность $\rho_4^{20}$ | 2 Фракционный состав 7 н. к. | 10% | 50% | 90% | 97,5% | 3 Групповой углеводородный состав 8 ароматические | 9 нафтеновые | 10 парафиновые | 11 непредельные | 12 Давление насыщенных паров при 38° мм рт. ст. | 13 Содержание серы, % | 4 Октановое число 5 моторный метод 14 без ТЭС | 15 с 0,8 мл/кг ТЭС | 16 авиационный метод с 1,3 мл/л ТЭС | 17 Сортность на богатой смеси с 1,3 мл/л ТЭС |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 18 Для получения авиабензина: | | | | | | | | | | | | | | | | |
| 115/145 . . . . . | 0,781 | 37 | 66 | 122 | 144 | 160 | 60 | 7 | 33 | 0 | 358 | — | — | — | 100 | > 160 |
| 100/130 . . . . . | 0,732 | 54 | 62 | 95 | 148 | 165 | 38 | 16 | 44 | 2 | 350 | — | 80,0 | | 100 | 130 |
| 95/130 . . . . . | 0,7482 | 45 | 62 | 101 | 142 | 169 | 37 | 10 | 51 | 2 | — | — | — | | 95 | 132 |
| 19 Для получения автомобильного бензина . . | 0,745 | 34 | 46,5 | 108 | 196 | 214,5 | 12 | 37 | | 51 | — | 0,06 | 79,5 | 85,9 | — | — |
| | 0,747 | 35 | 45,5 | 110 | 196 | 222 | 14 | 51 | | 35 | — | 0,26 | 80,2 | 85,0 | — | — |
| | 0,776 | 30,5 | 46,0 | 133 | 196 | 213 | 27 | 57 | | 16 | — | 0,04 | 83,5 | 89,0 | — | — |

1) Designation; 2) fractional composition; 3) group hydrocarbon composition; 4) octane number; 5) motor method; 6) density $\rho_4^{20}$; 7) start of boiling; 8) aromatic; 9) naphthenic; 10) paraffinic; 11) unsaturated; 12) pressure of saturated vapors at 38° mm Hg; 13) sulfur content, %; 14) without TES [TEL]; 15) with 0.8 ml/kg TES [TEL]; 16) aviation method with 1.3 ml/l TES; 17) rich-mixture grade with 1.3 ml/l TES; 18) for aviation gasoline; 19) for automotive gasoline.

rule, without the catalytic purification stage) can be used independently as an automotive gasoline, and its fraction boiling over between 180 and 205°, is used as a component in this gasoline.

The composition of the catalytic-cracking gasolines to some extent is a function of the initial crude, as well as of the process regime, but primarily, and this applies particularly to the gasolines of the second cracking stage, the composition of the [catalytic-cracking] gasolines is determined by the specific directions taken by the hydrocarbon reactions caused by the catalyst. Gasolines from the first [illegible]

contain a substantial quantity of unsaturated hydrocarbons, attaining 51% (Table 62), and relatively slightly branched paraffinic hydrocarbons. The content of aromatic hydrocarbons is greater than in direct-distillation and thermal-cracking gasolines. Despite the high content of unsaturated hydrocarbons, the catalytic-cracking gasolines of the first stage are rather stable in storage. This can be explained by the nature of the unsaturated hydrocarbons that are represented by the olefins in the dominant (basic) mass.

The octane numbers of catalytic-cracking gasolines of the first stage are higher than those for the basic mass of the direct-distillation gasolines as well as of the thermal-cracking gasolines.

The second stage catalytic-cracking gasolines obtained through the catalytic processing of the first-stage gasolines differ rather markedly from the latter in terms of chemical composition. Under the action of the catalyst, aromatization, isomerization, and hydrogenation of the unsaturated hydrocarbons take place, as a result of which their content in the gasoline is reduced to 1 – 2%, whereas the content of aromatic and isoparaffinic hydrocarbons increases. The latter are concentrated in the head gasoline fraction and amount to 90 – 95% of all the paraffinic hydrocarbons in the gasoline. The tailings are made up primarily of aromatic hydrocarbons. It is for this reason, unlike in the case of direct-distillation gasolines, as the end of boiling rises for catalytic-cracking gasolines their antiknock properties show virtually no impairment (see Fig. 110). This makes it possible to obtain gasolines having the maximum permissible (97.5%) gasoline boil off (180°). The presence of isoparaffinic hydrocarbons in the head portion of the gasoline is responsible for the low temperature at which 10% of the gasoline boils over (56 – 60°), and the presence of aromatic hydrocarbons in the tailings is responsible for the comparatively

high boil-off temperature for 90% gasoline (145 – 158°).

TABLE 63

Group Hydrocarbon Composition and Properties of Catalytic-Cracking Gas Oils [10]

| 1 Показатели | 2 Сырье каталитического крекинга | | | |
|---|---|---|---|---|
| | 3 парафинового основания | | 4 нафтено-ароматического основания | |
| | № 1 | № 2 | № 3 | № 4 |
| 5 Плотность $\rho_4^{20}$ | 0,849 | 0,856 | 0,892 | 0,897 |
| 6 Фракционный состав: | | | | |
| 7 н. к. | 242 | 225 | 252 | 187 |
| 10% | 248 | 246 | 264 | 241 |
| 50% | 259 | 269 | 293 | 267 |
| 90% | 282 | 324 | 323 | 310 |
| 8 к. к. | 305 | 346 | 347 | 341 |
| 9 Вязкость | 1,27 | 1,38 | 1,64 | 1,32 |
| Кислотность, мг КОН 10 | 0,24 | 4,48 | 1,34 | 1,52 |
| 11 Коксуемость, % | 0,046 | 0,019 | 0,011 | 0,088 |
| Температура застывания, °С 12 | —13 | —18 | —47 | —50 |
| 13 Групповой углеводородный состав: | | | | |
| ароматические 14 | 32,6 | 31,2 | 42,8 | 53,0 |
| 15 парафиновые | 53,2 | 49,4 | 46,7 | 28,5 |
| нафтеновые 16 | 11,0 | 14,4 | 6,2 | 14,0 |
| 17 Непредельные | 3,2 | 5,0 | 4,3 | 4,5 |
| Цетановое число 18 | 56 | 50,5 | 35 | 32 |

1) Indicators; 2) catalytic-cracking raw material; 3) paraffinic base; 4) naphthenic-aromatic base; 5) density, $\rho_4^{20}$; 6) fractional composition; 7) start of boiling; 8) end of boiling; 9) viscosity; 10) acidity, mg KOH; 11) cokability, %; 12) solidification temperature, °C; 13) group hydrocarbon composition; 14) aromatic; 15) paraffinic; 16) naphthenic; 17) unsaturated; 18) cetane number.

The combination of isostructural paraffinic hydrocarbons with aromatic hydrocarbons in catalytic-cracking gasolines determines their high antiknock properties in both lean and rich mixtures (see Table 62).

The composition and properties of catalytic-cracking gas oils are functions of the initial crude and the process regime (Table 63).

The gas oils obtained from a paraffinic-base crude are predominantly made up of paraffinic hydrocarbons. It is for this reason that they have comparatively high solidification temperatures. Gas oils obtained from a naphthenic-aromatic-base crude contain a large quant

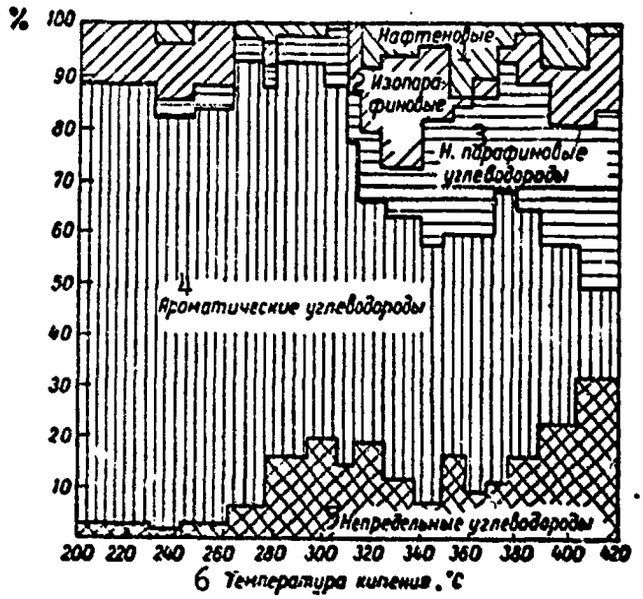


Fig. 113. Group hydrocarbon composition of narrow catalytic-cracking gas-oil fractions from heavy Romashkinskiy crude petroleum [1]. 1) Naphthenic; 2) isoparaffinic; 3) naphthenic-paraffinic hydrocarbons; 4) aromatic hydrocarbons; 5) unsaturated hydrocarbons; 6) boiling point, °C.

of aromatic hydrocarbons, predominantly bicyclic. Moreover, among the aromatic hydrocarbons in the catalytic-cracking gas oils, unlike the direct-distillation gas oils, there are hydrocarbons with three or more rings. For example, in the catalytic-cracking gas oil from the heavy Romashkinsky crude, for whose narrow fractions the group hydrocarbon composition is presented in Fig. 113, there are 6.5% monocyclic aromatic hydrocarbons, 30.2% bicyclic, 11.8% tricyclic, and 14.3% polycyclic [2].

Because of the high content of aromatic hydrocarbons in the catalytic gas oils and because of the high "cyclicity" [Tr. note: tsiklichnost', Russian word indicating the number of rings in a hydrocarbon] of these aromatic hydrocarbons, these gas oils have low cetane numbers.

Hydrogenation Products

Hydrogenation gasolines serve as base fuels for the production of aviation and automotive gasolines or are used directly as automotive gasolines. The higher-boiling hydrogenation products are used as base fuels for the production of diesel fuels and for fuels to be used in jet engines.

The composition and properties of hydrogenation gasolines are functions of the initial raw material, the conditions of the process, and the temperature limits of gasoline removal. Hydrogenation gasolines are close to direct-distillation gasolines in terms of the group hydrocarbon composition. The quantity of unsaturated hydrocarbons in the hydrogenation gasolines does not exceed 1 – 2%, and the content of aromatic hydrocarbons in these gasolines does not exceed 8 – 9%. Therefore, hydrogenation gasolines are stable in storage and have a low pour point.

The composition and properties of hydrogenation products boiling over above 180 – 205° are also functions of the nature of the crude and the conditions of the process.

Catalytic-Reforming Products

Since gasoline or light ligroin generally serves as the raw material for catalytic reforming, only gasoline is obtained as the basic product of the process, and this gasoline, depending on the initial raw material used as the catalyst and the conditions of the process, is used either as a base or commercial automotive gasoline or as a component in this commercial automotive gasoline, or as a component in aviation gasoline. Aromatization is the basic reaction of the process; therefore, in catalytic-reforming gasolines there is a large quantity of aromatic hydrocarbons, attaining 55% (Table 64) in the aviation-gasoline component, which is intended for the production of 115/145 aviation gasoline.

In view of the high content of aromatic hydrocarbons (33 – 45.5%), the catalytic-reforming products used for the production of automotive gasoline exhibit high antiknock properties; the octane number of the end gasoline is virtually independent of its fractional composition (see Fig. 110) and is only slightly dependent on the octane number of the initial raw material.

Synthesis Products from Carbon Monoxide and Hydrogen (Water Gas)

TABLE 64

Characteristic of Catalytic-Reforming Gasolines

| 1 Назначение | 5 Плотность $\rho_4^{20}$ | 2 Фракционный состав 6 н. к. | 10% | 50% | 90% | 7 к. к. | 8 Давление насыщенных паров при 38°, мм рт. ст. | 9 Содержание ароматических углеводородов, % | 10 Бромное число | 11 Сера, % | 3 Октановое число 4 моторный метод 12 без ТЭС | 13 с 0,8 мл/л ТЭС | 14 авиационный метод с 1,3 мл/л ТЭС | 15 Сортность на богатой смеси с 1,2 мл/л ТЭС |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 Компонент авиабензина 115/145 | 0,785 | — | — | — | — | — | 358 | 65 | 0 | — | — | — | 100 | 216 |
| Компонент авиабензина 100/130 | 0,777 | 55 | 70 | 105 | 154 | 175 | 360 | 52,0 | 16,1 | — | — | — | 90,8—99 | 166—177 |
| 17 | | | | | | | | | | | | | | |
| 18 Автомобильный базовый (Платформинг) | 0,747 | 38 | — | — | — | 240 | 550 | — | — | 0,006 | 75,7 | 83,7 | 80,6 | 92,3 |
| | 0,765 | 36 | — | — | — | 229 | 445 | — | — | 0,003 | 78,2 | 89,3 | 85,0 | 95,0 |
| 19 Автомобильный базовый (подвижный катализатор) | 0,758 | 72 | 89 | 118 | 159 | 201 | — | 33,6 | 8,2 | 0,01 | 85,4 | 94,9 | — | — |
| | 0,805 | 46 | 114 | 157 | 181 | 216 | — | 45,5 | 17,4 | 0,015 | 96,5 | 101,4 | — | — |

| 20 Октановое число (исследовательский метод) 21 Без ТЭС | 22 С 0,8 мл/л ТЭС |
|---|---|
| 80,6 | 92,3 |
| 85,0 | 95,0 |
| — | — |
| — | — |

1) Designation; 2) fractional composition; 3) octane number; 4) motor method; 5) density, $\rho_4^{20}$; 6) start of boiling; 7) end of boiling; 8) pressure of saturated vapors, at 38°, mm Hg; 9) content of aromatic hydrocarbons, %; 10) bromine number; 11) sulfur, %; 12) without TES [TEL]; 13) with 0.8 ml/l TES [TEL]; 14) aviation method, with 1.3 ml/l TES [TEL]; 15) rich-mixture grade, with 1.2 ml/l TES [TEL]; 16) component of 115/145 aviation gasoline; 17) component of 100/130 aviation gasoline; 18) automotive base (platforming); 19) automotive base (movable catalyst); 20) octane number (research method); 21) without TES [TEL]; 22) with 0.8 ml/l TES [TEL].

The synthesis products from carbon monoxide and hydrogen consist primarily of paraffinic and olefinic normal-structure hydrocarbons. The olefins are concentrated in the low-boiling fractions. The total content of olefins depends on the conditions of the process and the catalyst employed. With an increase in pressure, the content of olefins diminishes. In the higher-boiling fractions, there are virtually no olefins.

Because of the high content of normal paraffinic hydrocarbons, the gasolines obtained by synthesis from carbon monoxide and hydrogen have low octane numbers which drop sharply as the end-of-boiling of the gasoline rises (see Fig. 110). Fractions boiling over above 230 – 240° exhibit extremely high solidification temperatures and high cetane numbers.

Despite the large content of olefins, synthesis gasolines unlike thermal-cracking gasolines are stable in storage. This can be explained by the structure of the unsaturated compounds contained in these gasolines.

Because of low antiknock properties, gasoline obtained through synthesis from carbon monoxide and hydrogen are used only as components in automotive fuels. The higher-boiling fractions are also used only as components of diesel fuels, and here the end-of-boiling of these fractions must be restricted to 230 – 260° in the production of winter grades of diesel fuels.

FUEL COMPONENTS

Components are added to the base fuels to improve the antiknock and physicochemical properties of the fuels, as well as to increase fuel supplies.

Heavily branched paraffinic hydrocarbons or their mixtures – isopentane, alkylate, industrial isooctane – are used as gasoline com...

ents; aromatic hydrocarbons or their mixtures – benzene, toluene, xylenes, ethyl benzene, isopropylbenzene (cumene), pyrobenzene, and alkylbenzenes; the oxygen-containing compounds are ethyl alcohol, isopropyl ether, and acetone.

Mixtures of hydrocarbons or individual compounds having high octane numbers (from 90 and higher without ethyl fluid) and grades (from 140 – 150 and higher with 3 – 4 ml/kg ethyl fluid) are used as components for aviation gasolines, as are hydrocarbons or their mixtures exhibiting a lightened fractional composition and increased vapor pressure.

Direct-distillation, thermal- or catalytic-cracking, and catalytic-reforming gasolines may serve as components of automotive gasolines, as can polymer- and alkyl-gasolines. In addition, the tail and head fractions of direct-distillation gasolines left over in the production of aviation gasolines are used as components in automotive gasolines, as are "gas" gasoline, the spent butane-butylene cracking-gas fraction, the penta-amylene fraction, and isopentane.

Direct-distillation and thermal- and catalytic-cracking ligroins and kerosenes serve as components in tractor fuels.

The products derived in the synthesis from carbon monoxide and hydrogen, as well as catalytic- and thermal-cracking gas oil can serve as diesel-fuel components.

Components have found their greatest application primarily for the improvement of antiknock and physicochemical properties in the production of aviation gasolines. In the production of other types of fuels, components are intended primarily to provide for an increase in the fuel supply. In addition, certain improvements in fuel properties can be achieved.

Table 65 shows the mean values of the physicochemical and anti-

knock properties of the components in the aviation and automotive gasolines.

During the production of aviation gasolines, the components are added together with the ethyl fluid. B-70 gasoline, produced in comparatively limited quantities, is an exception. Therefore, given the characteristic of the components used in aviation gasolines, their capacity to improve the antiknock properties of the base gasolines is considered from the standpoint that ethyl fluid is present. The antiknock effectiveness of the automotive components is presented without consideration of ethyl fluid.

Aviation-Gasoline Components

Isoparaffinic hydrocarbons

The isoparaffinic hydrocarbons used as components differ significantly from other classes of hydrocarbons in terms of the physicochemical properties which govern the operational characteristics of the gasolines. For example, these have the greatest heat of combustion among all classes of hydrocarbons, the lowest hygroscopicity, density, surface tension, latent heat of vaporization, and viscosity.

As these [isoparaffinic hydrocarbons] are added to the base gasolines for purposes of improving the antiknock properties of the latter, the above-enumerated physicochemical properties of the gasolines undergo change and, consequently, so do the operational properties of these gasolines. However, with a slight exception due to the fact that the direct-distillation gasolines contain primarily only paraffinic and naphthenic hydrocarbons, and considering that the content of paraffinic hydrocarbons reaches 60 – 65% in the catalytic-process gasolines, these changes are comparatively insignificant. There are more significant changes in such physicochemical properties as vapor tension and the fractional composition. In this case, if the change in

TABLE 69

Properties of Components in Aviation and Automotive Gasolines

| 1 Наименование | 2 Плотность $d_4^{20}$ | 3 Фракционный состав: н. к. | 10% | 50% | 90% | 97.5% | 6 Температура застывания, °С | 7 Давление насыщенных паров при 38°, мм рт. ст. | 8 Теплота сгорания (высшая), ккал/кг | 9 Поверхностное натяжение при 20°, эрг/см² | 10 Скрытая теплота испарения, ккал/кг | 11 Вязкость динамическая при 20°, сантипуазы | 4 Антидетонационные свойства: 12 октановое число без Р-9 (моторный метод) | 13 октановое число с 4 мл/кг Р-9 | 14 сортность с 4 мл/кг Р-9 на богатой смеси |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 15 Изопентан | 0,616—0,640 | 24—30 | 28—31 | 28—35 | 29—73 | 31,5—120 | −159,6 | 954—1080 | 11 020 | 13,7 | 85 | 0,280 | 90 | 105,6—110 | 142—144 |
| 16 Изооктан технический | 0,692—0,711 | 93—96,5 | 82—101 | 98,5—115 | 100,6—115 | 117—186 | — | 97—200 | 11 200 | 20 | 75 | 0,500 | 89—90 | 104,5—106,5 | 145 |
| 17 Алкилат | 0,688—0,715 | 54—62 | 82—102 | 105—113 | 114—140 | 171—188 | — | 115—208 | 11 200 | | 75 | | 90—95 | 105—107 | 143 |
| 18 Бензол | 0,889 | 80 | 80 | 80 | 80 | 81 | +5,4 | 75 | 10 000 | 28,8 | 95 | 0,651 | 100 | 97 | — |
| 19 Пиробензол | 0,8500—0,870 | 80—90 | 85—97 | 98—112 | 142—155 | 161,5—180 | −20—(−33) | — | 10 200 | — | — | — | 84—91,3 | 92—96,5 | — |
| 20 Толуол | 0,885 | 110 | 110 | 110 | 110 | 111 | −94,5 | 20 | 10 150 | 28,4 | 90 | 0,583 | 100 | 105,5 | 250 |
| 21 Этилбензол | 0,884 | 136 | 136 | 136 | 136 | 136,5 | −93 | 6,8 | 10 280 | 29,2 | 81 | 0,668 | 96 | 102 | 285 |
| 22 Изопропилбензол | 0,858 | 152 | — | — | — | 152,5 | −96,9 | — | ~10 300 | — | 85 | ~0,860 | 99 | 99 | 285 |
| 23 Алкилбензол | 0,857—0,868 | 105—144 | 119—144 | 140—167 | 154—180 | 167—182 | — | — | — | — | — | — | 94,2—95 | — | > 160 |
| 24 «Головка» прямой гонки | — | 28 | 36 | 56 | 123 | 151 | −60 | 784 | — | — | — | — | 72,8 | — | — |
| 25 Отработанная бутан-бутиленовая фракция | 0,580—0,610 | — | — | — | — | — | < −60 | 1500—2000 | — | — | — | — | 90—95 | — | — |
| 26 Алкилбензины | 0,695 | 30—46 | 98 | 107 | 128 | 162—174 | < −60 | 228 | — | — | — | — | 88—89 | — | — |
| 27 Газовый бензин | — | 33 | 89 | 47 | 97 | 153 | < −60 | 662 | — | — | — | — | — | — | — |
| 28 Полимербензин | 0,730 | 40 | — | — | — | 200 | < −60 | 350 | — | — | — | — | 83—85 | — | — |
| 29 Пента-амиленовая фракция | 0,635—0,645 | 23—28 | 30 | 40 | 65 | 110—130 | < −60 | 1000—1200 | — | — | — | — | 70 | — | — |

Key to Table 65: 1) Designation; 2) density, $\rho_4^{20}$; 3) fractional composition; 4) antiknock properties; 5) start of boiling; 6) solidification temperature, °C; 7) pressure of saturated vapor at 38°, mm Hg; 8) heat of combustion (uppermost), kcal/kg; 9) surface tension at 20°, erg/cm$^2$; 10) latent heat of vaporization, kcal/kg; 11) dynamic viscosity at 20°, centipoises; 12) octane number without P-9 (motor method); 13) octane number with 4 ml/kg of P-9; 14) grade with 4 ml/kg of P-9, in rich mixture; 15) isopentane; 16) technical isooctane; 17) alkylate; 18) benzene; 19) pyrobenzene; 20) toluene; 21) ethyl benzene; 22) isopropylbenzene; 23) alkylbenzene; 24) direct-distillation "head"; 25) butane-butylene fraction; 26) alkyl gasoline; 27) "gas" gasoline; 28) polymer gasoline; 29) penta-amylene fraction.

TABLE 66

Fractional Composition and Vapor Pressure of Gasolines Containing Isopentane

| 1 Бензин | 2 Фракционный состав | | | | | 3 Давление насыщенных паров при 38°, мм рт. ст. |
|---|---|---|---|---|---|---|
| | 4 н. к. | 10% | 50% | 90% | 97,5% | |
| Б-70 5 | 82 | 92 | 103,5 | 125,5 | 149 | 128 |
| 95% Б-70+5% изопентана 6 | 59 | 85,5 | 102 | 123 | 147 | 161 |
| 90% Б-70+10% изопентана 7 | 58.5 | 77 | 100,5 | 123 | 143 | 225 |
| 85% Б-70+15% изопентана 8 | 52 | 70 | 98,5 | 122 | 143 | 262 |
| 80% Б-70+20% изопентана 9 | 49 | 65 | 96,5 | 121 | — | 297 |
| 75% Б-70+25% изопентана 10 | 44 | 58 | 95 | 123 | 142 | 353 |
| Базовый бензин 11 | 67 | 87 | 102 | 130 | 161 | 199 |
| 95% бензина+5% изопентана 12 | 54,5 | 79 | 101 | 129 | 159 | 243 |
| 13 90% бензина+10% изопентана | 55,5 | 74 | 99,5 | 128 | — | 291 |
| 14 85% бензина+15% изопентана | 45 | 67 | 98,5 | 126,5 | 157 | 335 |
| 15 80% бензина+20% изопентана | 42 | 60.5 | 94,5 | 124,5 | 151 | 367 |
| 16 75% бензина+25% изопентана | 39 | 56 | 92,0 | — | 154 | 406 |

1) Gasoline; 2) fractional composition; 3) pressure of saturated vapors, at 38°, mm Hg; 5) B-70; 6) 95% B-70 + 5% isopentane; 7) 90% B-70 + 10% isopentane; 8) 85% B-70 + + 15% isopentane; 9) 80% B-70 + 20% isopentane; 10) 75% B-70 + 25% isopentane; 11) base gasoline; 12) 95% gasoline + 5% isopentane; 13) 90% gasoline + 10% isopentane; 14) 85% gasoline + 15% isopentane; 15) 80% gasoline + 20% isopentane; 16) 75% gasoline + 25% isopentane.

the heat of combustion and hygroscopicity is comparatively a weak function of the nature of the isoparaffinic component that is added, the change in vapor tension and fractional composition will be a very strong function of the particular component that has been added to the base gasoline. Any change in the antiknock properties of the base g

olines is also governed by the nature of the isoparaffinic component.

Below we present changes in the most important physicochemical properties of base gasolines as the isoparaffinic components presently in use are added to these gasolines.

Isopentane

The composition of industrial isopentane is a function of the care exercised in the rectification process employed in the separation of the isopentane. Generally, the content of the isopentane (2-methylbutane) in the industrial product ranges between 80 and 95%, and the remaining 5 to 20% are made up of n-pentane and higher-boiling hydrocarbons.

As can be seen from the data presented in Table 9, isopentane, having a high octane number, has a low boiling point and extremely high vapor tension. Its grade is comparatively low. Isopentane is used when it is necessary simultaneously to improve the octane number of the base fuel and the volatility of the base fuel, or only to improve the volatility (Table 66). However, because of the high vapor tension, 5 – 20% is added.

Industrial Isooctane

The composition of industrial isooctane is not constant and is a function of the composition of the raw material used for polymerization, as well as being a function of the catalyst employed and the conditions of polymerization. The composition of industrial isooctane determines its properties as well, and these, as can be seen from Table 65, vary within a very wide range. High vapor tension, high 50%-boil-off temperatures, and particularly for the 10% product, as well as comparatively high octane numbers and relatively low grades, are characteristic of industrial isooctane.

As can be seen from Tables 67 and 68, industrial isooctane sub-

TABLE 67

Octane Numbers of Gasoline Mixtures (with 3 ml/kg of P-9) with Various Industrial Isooctanes [11]

| 1 Состав смеси, % | | 2 Изооктан 90 | | | 3 Изооктан 100 | | |
|---|---|---|---|---|---|---|---|
| 4 технический изооктан | 5 базовый бензин | 6 бензин с октановым числом | | | 7 бензин с октановым числом | | |
| | | 84 | 87 | 90 | 84 | 87 | 90 |
| 0 | 100 | 84 | 87 | 90 | 84 | 87 | 90 |
| 10 | 90 | 86 | 89 | 91 | 86 | 89 | 92 |
| 20 | 80 | 88 | 90 | 93 | 83 | 91 | 94 |
| 30 | 70 | 90 | 92 | 94 | 91 | 93 | 96 |
| 40 | 60 | 92 | 93 | 96 | 94 | 96 | 98 |
| 50 | 50 | 93 | 95 | 98 | 97 | 100 | 100 |

1) Composition of mixture, %; 2) isooctane 90; 3) isooctane 100; 4) industrial isooctane; 5) base gasoline; 6) gasoline with the following octane number; 7) gasoline with the following octane number.

TABLE 68

Grade of Base-Gasoline Mixtures with Industrial Isooctane

| 1 Базовый бензин | 2 Групповой углеводородный состав | | | 3 Сортность с 4 мл/кг Р-9 при содержании изооктана, % | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 4 ароматические | 5 нафтеновые | 6 парафиновые | 0 | 10 | 20 | 30 | 40 | 50 | 100 |
| № 1 | 6 | 44 | 50 | 96 | 96 | 98 | 100 | 104 | 110 | 144 |
| № 2 | 13 | 41 | 46 | 98 | 99 | 101 | 105 | 110 | 116 | |
| № 3 | 14 | 55 | 31 | 123 | 126 | 128 | 130 | — | — | |

1) Base gasoline; 2) group hydrocarbon composition; 3) grade with 4 ml/kg of P-9, given the following isooctane content, in %; 4) aromatic; 5) naphthenic; 6) paraffinic.

stantially improves the octane number of the base gasolines and has a very weak effect on grade.

Alkylate

Like the industrial isooctane, the alkylate composition is not constant and is a function of the catalyst employed in the alkylation of the unsaturated hydrocarbon, and it also depends on the conditions

under which the process was executed.

Alkylate, like industrial isooctane, substantially raises the octane number of the base gasolines and raises the grade of these gasolines only slightly. Alkylate and industrial isooctane are virtually identical with respect to the change they exert on the antiknock properties of the base fuels.

Aromatic hydrocarbons

In terms of their physicochemical properties, aromatic hydrocarbons are quite different from the remaining classes of hydrocarbons in fuel compositions. They have higher boiling points, density, surface tension, latent heat of vaporization, and viscosity; they exhibit greater hygroscopicity, they have a more pungent odor, and also exhibit more pronounced toxic properties. The carbon-to-hydrogen ratio in these hydrocarbons is the greatest and as a result the mass heat of combustion and theoretical air flow rate for total (complete) combustion are at their lowest.

Some of the aromatic hydrocarbons have high melting points (benzene, n-xylene).

The behavior of aromatic hydrocarbons is unique in combustion engines. Their combustion is accompanied by increased thermal stresses in the engine and by scale formation, as a result of which autoignition of the fuel takes place. Aromatic hydrocarbons are sensitive to the temperature regime of the engine, and as a result the antiknock properties of these hydrocarbons are impaired as the temperature of the working mixture or coolant rises. All aromatic hydrocarbons are completely soluble in other classes of hydrocarbons.

Since direct-distillation and hydrogenation gasolines, to which aromatic components are added, primarily consist of paraffinic and naphthenic hydrocarbons, and further since they generally do not con-

tain more than 5 – 9% aromatic hydrocarbons, the addition of the latter brings about rather pronounced changes in the physicochemical and operational properties of the gasolines.

1. There is an increase in density, viscosity, and surface tension of the gasolines, as a result of which a slight change in the operating conditions of the carburetor takes place – the fuel-feed is reduced and the diameter of the fuel drops increases, i.e., fuel atomization and, consequently, fuel vaporizability are impaired.

2. The fractional composition of the gasolines becomes heavier and as a result there is a reduction in the degree of fuel vaporization, the starting properties of the fuel are impaired, as are the conditions for combustion within the engine.

3. There is some increase in the latent heat of vaporization of the gasoline, which results in a temperature drop across the fuel line, the latter due to vaporization.

4. The toxic properties of the gasoline increase and the odor of the fuel worsens.

5. In a number of cases, there is an increase in the pour point of the gasolines.

6. There is a change in the quantity of air theoretically required for complete combustion, i.e., there is a change in the composition of the working mixture.

7. The hygroscopicity of the gasolines increases, and there is an increase in the associated danger of the settling out of ice crystals from these gasolines at low air temperatures.

8. The tendency to scale formation and the appearance of autoignition increases.

Consequently, the addition of aromatic hydrocarbons to the gasolines in order to improve the antiknock properties of the gasolines

brings about the simultaneous impairment of almost all the operational properties of the gasolines. The degree of impairment is determined by the quantity of aromatic hydrocarbons added, and by the nature of these hydrocarbons. All of the aromatic hydrocarbons do not impair the operational properties of the gasolines equally. Below we present a characteristic of the aromatic hydrocarbons and their mixtures, used as aviation-gasoline components.

Benzene, pyrobenzene

High-purity-coal and petroleum benzene is used as a component in aviation gasolines. When benzene is added to gasolines, the antiknock properties of the gasolines are improved, and here the effect is greater in the case of a rich mixture than in the case of a lean mixture. The change in grade through the addition of benzene depends, in great measure, on the chemical composition of the gasoline.

The octane numbers of gasolines containing 3 – 4 ml/kg of ethyl fluid, even with the addition of 40 – 50% benzene, increased by only 2 – 3 units, and with the addition of 15 – 20% benzene, only by 1 – 2 units. For example, the octane number of a gasoline containing 3 ml/kg ethyl fluid, after the addition of 20% benzene, increased only from 86.1 to 87.5.

Benzene, as a rule, is used in the production of B-70 gasoline, which contains no ethyl fluid. However, in this case as well the addition of benzene is generally restricted to 5 – 10%, since any further increase in the quantity of benzene in the mixture results in a pronounced rise in the pour point of the gasolines. With the addition of 20% of benzene, the pour point of the gasoline rises to -41.5 – 42° and exceeds the permissible limits.

The addition of benzene lightens the fractional composition of the gasolines, particularly of the 50 and 90% gasolines. Depending on

its magnitude, the temperature required for the boiling off of 10% of a gasoline either drops or rises with the addition of benzene.

Of all the aromatic components, benzene exhibits the least heat of combustion, the greatest latent heat of vaporization, as well as the highest surface tension, viscosity, and hygroscopicity; the latter undergoes a particularly pronounced increase in comparison with the nonaromatic gasolines as the temperature rises. Benzene is more toxic than other aromatic components, and it is more sensitive than these other aromatic components to temperature during engine combustion, and it has a greater tendency to scale formation. Therefore, when benzene is added to base gasolines, in addition to a rise in the pour point, the most pronounced changes (in comparison with the remaining aromatic components) in the above-mentioned operational properties of the gasolines take place.

In addition to pure benzol, industry also produces an industrial mixture – pyrobenzene [motor benzol] (see Table 65), which is a pyrolisis product and consists of a mixture of benzene, xylenes, and the higher-boiling aromatic hydrocarbons and certain quantities of unsaturated hydrocarbons and hydrocarbons of other classes.

Pyrobenzene [motor benzol] comes in two grades: without toluene, and a pour point of $-12^{\circ}$ and a lightened grade, i.e., containing a greater percentage of benzene, with a pour point of $0^{\circ}$. Since there are up to 10 – 15% hydrocarbons of other classes in addition to the aromatic hydrocarbons in pyrobenzene, the antiknock properties of the motor benzol itself, as well as of its mixtures, are lower than in the case of benzene. The permissible content of pyrobenzene ranges from 15 to 20%, since if it were present in greater quantities its pour point would exceed the permissible limits established by the GOST [All-Union State Standards]. The fractional composition of the base

gasolines, given this pyrobenzene content, becomes insignificantly heavier. Other operational properties are impaired to a somewhat lesser degree as a result of the addition of pyrobenzene, than would be the case with the addition of benzene.

**Toluene**

TABLE 69

Change in Antiknock Properties of Gasolines, with the Addition of Toluene

| 1 Продукты | 2 Антидетонационные свойства с 4,0 мл/кг Р-9 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 3 октановое число при содержании толуола, % | | | | 4 сортность на богатой смеси при содержании толуола, % | | | | | |
| | 0 | 15 | 30 | 50 | 0 | 15 | 25 | 30 | 35 | 50 |
| 5 Смесь: 85% изооктана + 15% н-гептана . . | — | — | — | — | 107 | 132 | 147 | — | 164 | — |
| 6 Смесь: 70% изооктана + 30% н-гептана . . | 98,2 | 90,8 | 93,4 | 95,8 | 92 | 98 | — | 119 | — | 160 |
| 7 Базовый бензин № 1 . . . . . | 91,5 | 92,2 | 93,7 | 95,4 | 102 | 119 | — | 141 | — | > 160 |
| 8 Базовый бензин № 2 . . . . . | 93,8 | 94,2 | 95,8 | 96,4 | 130 | 143 | — | 160 | — | — |

1) Products; 2) antiknock properties with 4.0 ml/kg P-9; 3) octane number with a toluene content of, %; 4) rich-mixture grade, with a toluene content of, %; 5) mixture: 85% isooctane + 15% n-heptane; 6) mixture: 70% isooctane + 30% n-heptane; 7) base gasoline No. 1; 8) base gasoline No. 2.

TABLE 70

Change in the Fractional Composition of Gasolines with the Addition of Toluene

| 1 Бензин, % вес. | 2 Толуол, % вес. | 3 Фракционный состав | | | | |
|---|---|---|---|---|---|---|
| | | 4 н. к. | 10% | 50% | 90% | 97,5% |
| 5 Базовый бензин (№ 1) | | | | | | |
| 100 | 0 | 47 | 69 | 100,5 | 141 | 163 |
| 85 | 15 | 51 | 70 | 102 | 133 | 162 |
| 70 | 30 | 52 | 74 | 104 | 128 | 160,5 |
| 50 | 50 | 56 | 84 | 105 | 121 | 156 |

TABLE 70 (Continued)

| 6 Базовый бензин (№ 2) | | | | | | |
|---|---|---|---|---|---|---|
| 100 | 0 | 68 | 85 | 95 | 119 | 145 |
| 85 | 15 | 80 | 89 | 98,5 | 116,5 | 143 |
| 70 | 30 | 82 | 92,5 | 99 | 115,5 | 139 |
| 50 | 50 | 84 | 96,5 | 101,5 | 111,5 | 129,5 |

1) Gasoline, % by weight; 2) toluene, % by weight; 3) fractional composition; 4) start of boiling; 5) base gasoline (No. 1); 6) base gasoline (No. 2).

Toluene is produced industrially with a high degree of purity, and it may therefore be regarded as virtually an individual hydrocarbon (see Table 65).

Table 69 presents data on the change in the antiknock properties, and Table 70 presents data on the change in the fractional composition of various gasolines as a result of the addition of toluene to these gasolines.

As can be seen from the data presented in Table 69, toluene improves the gasoline grade more effectively than it does the octane number of the gasoline.

With the addition of toluene, the fractional composition of the 10 and 50% gasolines becomes heavier. The boiling range of the 50% gasoline fraction rises less significantly. The boiling temperature for 90% gasoline, with the addition of toluene, naturally drops all the more markedly, the higher the temperature.

Toluene is used primarily to improve the antiknock properties of rich-mixture gasolines. The remaining operational properties of gasolines are impaired with the addition of toluene, although less significantly than in the case of benzene being added.

Ethyl benzene, isopropylbenzene, alkylbenzene

Depending on the composition of the gas employed for the alkylation of benzene, and also depending on the nature of the catalyst and

the conditions of alkylation, as well as on the temperature regime and the care exercised in rectification, either almost individual aromatic hydrocarbons (ethyl benzene, isopropylbenzene) or mixtures of various alkylated benzenes (alkylbenzenes) are obtained. The properties of the benzene-alklylation products are determined by their composition and vary within a wide range (see Table 65). The change in the physico-chemical and antiknock properties of the base gasolines, resulting from the addition of alkylbenzene to these gasolines, is a function of the properties and the composition of both the base gasolines and the alkylbenzene. Table 71 shows data on the change in the fractional composition of various base gasolines, resulting from the addition of various compositions of alkylbenzes to these gasolines.

We can see from these data that with the addition of alkylbenzene, there is a pronounced rise in the temperature at which the 10, 50, and 90% gasolines boil off. Depending on the fractional composition of the base gasolines and the alkylbenzene, the content of alkylbenzene in commercial gasoline is limited to 5 – 10% and a maximum of 15 – 25%.

With the addition of alkylbenzene or the individual aromatic hydrocarbons of its components to the base gasolines, the antiknock properties of the gasolines are improved more effectively than in the case of benzene, pyrobenzene, or toluene being added. In this case the effectiveness of the aromatic hydrocarbon with respect to improving the grade of the base gasolines depends on the magnitude of the side chain bound to the aromatic ring and in particular on the structure of the chain. With the branching of the side chain, the effectiveness of the aromatic hydrocarbon rises sharply.

The capacity of the alkylbenze effectively to improve the antiknock properties of lean- and rich-mixture base gasolines makes it possible, despite the restrictions on the addition of the alkylbenzene,

TABLE 71

Change in the Fractional Composition of Base Gasolines with the Addition of Alkylbenzenes to these gasolines [12 – 14]

| № п/п | 1 Бензины | 2 Фракционный состав | | | | |
|---|---|---|---|---|---|---|
| | | 3 н. к. | 10% | 50% | 90% | 97,5% |
| 1 | Ишимбайский . . 4. . . . | 49 | 70 | 99 | 133 | 147 |
| | Ишимбайский + алкилбензол № 1: 5 | | | | | |
| | 80% + 20% . . . . . | 50 | 73 | 107 | 144 | 165 |
| | 70% + 30% . . . . . | 50 | 73,5 | 112 | 149 | 167 |
| | 60% + 40% . . . . . | 50 | 75 | 120 | 155 | 169 |
| 2 | Грозненский 6. . . . . | 45 | 71 | 99,5 | 128 | 141 |
| | Грозненский + алкилбензол № 2: 7 | | | | | |
| | 90% + 10% . . . . . | 56 | 77,5 | 105,5 | 138 | 161,5 |
| | 70% + 30% . . . . . | 60 | 83 | 117 | 150 | 168 |
| | 60% + 40% . . . . . | 62 | 88 | 122 | 154,5 | 173 |
| 3 | «Экстра» . . . . . 8. | 65 | 79,5 | 51 | 107 | 127 |
| | 60% «Экстра» + 40% алкилбензола № 2 . . 9. | 67,5 | 88,5 | 113 | 148 | 169 |
| 4 | Б-70 . . . . . 10. . . | 47 | 69 | 100,5 | 141 | 163 |
| | Б-70 + алкилбензол № 3: 11 | | | | | |
| | 85% + 15% . . . . . | 53 | 73 | 104 | 143 | 163,5 |
| | 70% + 30% . . . . . | 53 | 77,5 | 110 | 145,5 | 165 |
| | 50% + 50% . . . . . | 63 | 89 | 118 | 147,5 | 166 |
| 5 | Бензин Б-74 . . . . 12. | 54 | 71,5 | 90,5 | 129 | 151,5 |
| | 60% Б-74 + 40% алкилбензола № 4 . . . . . 13. | 61 | 83 | 115 | 152 | 163 |

1) Gasolines; 2) fractional composition; 3) start of boiling; 4) Ishimbay; 5) Ishimbay + + alkylbenzene No. 1; 6) Groznyy; 7) Groznyy + alkylbenzene No. 2; 8) "Ekstra"; 9) 60% "Ekstra" + 40% alkylbenzene No. 2; 10) B-70; 11) B-70 + alkylbenzene No. 3; 12) B-74 gasoline; 13) 60% B-74 + 40% alkylbenzene No. 4.

to use it (the alkylbenzene) to improve the antiknock properties of gasolines simultaneously for both. However, in addition to the above-mentioned fact that the fractional composition becomes heavier, the addition of alkylbenzene impairs the remaining operational properties of the gasolines. Particular stress should be placed on the pungent and unique odor of alkylbenzene which is also important to the gasoline, even if the alkylbenzene is added in only small quantities.

Automotive-Gasoline Components

The components of automotive gasolines are examined in detail in

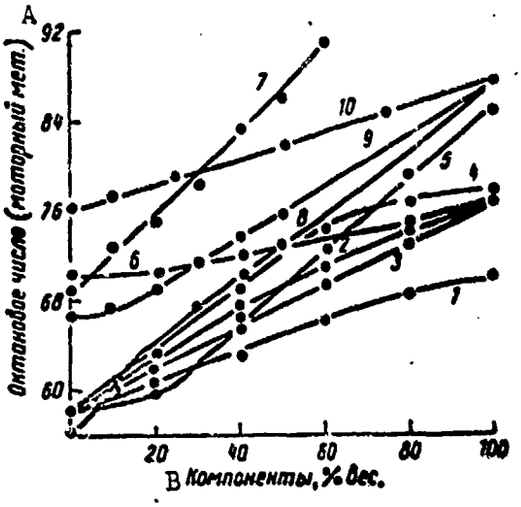


Fig. 114. Change in octane numbers in the case of gasoline mixing (motor method) [5]. 1) Direct-distillation gasoline with thermal-cracking gasoline; 2) direct-distillation gasoline with catalytic-cracking gasoline; 3) direct-distillation gasoline with catalytic-reforming gasoline; 4) direct-distillation gasoline with polymer gasoline; 5) direct-distillation gasoline with benzene; 6) thermal-cracking gasoline with catalytic-reforming gasoline; 7) direct-distillation gasoline with isopropylbenzene; 8) direct-distillation gasoline with alkylgasoline; 9) thermal-cracking gasoline with alkylgasoline; 10) catalytic-cracking gasoline with alkylgasoline. A) Octane number (motor method); B) components, % by weight.

Chapter 17.

Here, however, we will take note of the following. As direct-distillation, thermal- and catalytic-cracking, as well as catalytic-reforming, polymer- and alkylgasoline are mixed, no significant change in the fractional composition is observed. With the addition of spent butane butylene and penta-amylene fractions, and the addition of isopentane, "gas" gasoline, and the head fractions of direct-distillation gasoline to the enumerated gasolines, the fractional composition of the latter is lightened and the pressure of the saturated vapors is increased. The pressure of the saturated vapors experiences the most pronounced increase with the addition of the penta-amylene, and particularly, with the addition of the spent butane-butylene fractions. Therefore these are contained in quantities not exceeding 1 – 2% in the final gasoline product. In case the tail fractions of direct-distillation gasoline are added, the fractional composition of the gasolines becomes heavier.

The antiknock properties of automotive gasolines are evaluated (estimated) in terms of octane numbers which are determined either by

the motor or research methods. The nature of the change occurring in octane numbers as a result of the mixing of automotive-gasoline components depends on the group hydrocarbon composition of the components and the amount of component contained in the mixture. This is clearly demonstrated by the data shown in Fig. 114.

When mixing direct-distillation gasolines, i.e., gasolines consisting of paraffinic and naphthenic hydrocarbons, we find that the octane number of these gasolines changes additively. In mixing direct-distillation gasolines with thermal- and catalytic-cracking and particularly with polymer gasolines, i.e., with products containing unsaturated hydrocarbons or consisting of unsaturated hydrocarbons (polymer gasoline) we find that the octane numbers of the mixtures are higher than those calculated in accordance with the rule of additivity. Conversely, when direct-distillation gasolines are mixed with components consisting primarily of such aromatic hydrocarbons as benzene, toluene, xylenes (pyrobenzene), the resultant mixtures have lower octane numbers than those calculated in accordance with the rule of additivity. In adding isopropylbenzene to direct-distillation gasolines, we find an additive change in the octane number. The change in the octane number is almost additive in the case of direct-distillation gasolines mixed with catalytic-reforming gasolines.

When alkylgasoline is mixed with direct-distillation gasolines, the octane numbers of the mixtures are higher than those calculated, and when alkylgasoline is mixed with thermal- and catalytic-cracking gasolines, the octane number is lower than that calculated.

The greatest deviation from additivity in the case of mixing is observed with the addition of a small quantity of a high-octane component.

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## Chapter 14

## MOTOR-FUEL ADDITIVES

Additives are substances added to a fuel in small quantities to improve its operational properties.

At the same time, a single additive may have a complex action, i.e., improve not one, but two or more operational properties of the fuel.

One or more additives may be added to a fuel of a given type. As a rule, additives are mixed into the fuel in quantities ranging from thousandths to hundredths of a percent; for certain types of fuels, additives are required in concentrations reaching 1-2% and more.

The action of additives is based on their participation in the mechanism of processes that take place when the fuels are used; their concentrations in the fuels are too small for the properties of the additives to be added to those of the fuels.

The general specifications [1] set forth for additives reduce to the following: 1) the additives must be effective in small concentrations; 2) they must burn completely without formation of deposits on the engine's components; 3) they may not have a detrimental influence on any properties of the fuels; 4) they must be thoroughly soluble in the fuel and its components and only slightly soluble in water; 5) they must be stable (not decompose) under operational conditions; 6) they must be plentifully available and their cost must not be high.

At the present time, the use of fuel additives is a particularly important factor in view of the increased demand for fuels and the

"harder" conditions under which they are used in the engines.

Additives enable us to produce a fuel conforming to the demands of the contemporary engine from second-quality raw materials, which the industry is obliged to use in order to meet the growing demand for fuel. Additives have already come into commercial use to improve combustion of fuels, raise its chemical stability, lower its corrosive activity, reduce scale formation, and improve the properties of the fuels at low temperatures; dispersing and other additives are also employed.

Research and tests on new types of additives are being conducted; these include multifunctional and mixed additives, use of which is acquiring great importance.

ADDITIVES THAT IMPROVE THE MOTOR PROPERTIES OF FUELS

These additives include substances added to the fuel to improve the actual combustion process of the fuel in the engine. Antiknock compounds, which belong in this group of substances, are considered in a special chapter as additives that have come into particularly widespread use.

Additives that Improve Combustion of Diesel and Jet Fuels

Additives that accelerate the preflame oxidation of the fuel are used to improve combustion of fuel in diesel engines. Certain nitro and peroxide compounds have been found most effective for this purpose (Table 72).

Other additives that may be used to improve cetane number are carbamates (e.g., isopropylmethylnitrocarbamate) and certain compounds of metals (for example, sodium) [22]. The first amounts of additives raise the cetane number more than do subsequent amounts, although the optimum additive concentration is rather high (from 0.1 to 1-2% by volume).

TABLE 72

Increase in Cetane Number of Diesel Fuels Achieved by the Use of Certain Additives [2]

| 1 Присадки | 2 Цетановое число топлива | 3 Концентрация присадки, % | 4 Повышение цетанового числа при добавлении присадки |
|---|---|---|---|
| 5 *втор*-Нитропропан | 46,0 | 2,0 | 19,7 |
| 6 Динитропропан | 31,0 | 1,0 | 14,4 |
| 7 Нитробутан | 46,0 | 2,0 | 5,1 |
| 8 Нитрооктан | 46,0 | 2,2 | 3,8 |
| 9 Этилнитрат | 55,0 | 2,0 | 19,0 |
| 10 Бутилнитрат | 44,0 | 1,5 | 19,0 |
| 11 Амилнитрат | 44,0 | 1,5 | 23,0 |
| 12 Гексилнитрат | 39,1 | 1,5 | 17,6 |
| 13 Октилнитрат | 39,1 | 1,5 | 20,3 |
| 14 Нонилнитрат | 39,1 | 1,5 | 13,3 |
| 15 Этилнитрит | 46,0 | 2,0 | 16,7 |
| 16 Изоамилнитрит | 46,0 | 2,0 | 16,7 |
| 17 Перекись бутила | 39,1 | 1,5 | 20,2 |
| 18 Перекись гептила | 49,3 | 1,5 | 16,1 |
| 19 Перекись ди-*трет*-бутила | 55,9 | 1,0 | 15,2 |
| 20 н-Дибутиловый эфир | 39,1 | 1,5 | 7,5 |
| 21 Ацетальдегид | 39,1 | 1,5 | 3,5 |

1) Additive; 2) cetane number of fuel; 3) additive concentration, %; 4) increase in cetane number on addition of additive; 5) sec-nitropropane; 6) dinitropropane; 7) nitrobutane; 8) nitrooctane; 9) ethyl nitrate; 10) butyl nitrate; 11) amyl nitrate; 12) hexyl nitrate; 13) octyl nitrate; 14) nonyl nitrate; 15) ethyl nitrite; 16) isoamyl nitrite; 17) butyl peroxide; 18) heptyl peroxide; 19) di-tert-butyl peroxide; 20) n-dibutyl ether; 21) acetaldehyde.

Apart from raising the fuel's cetane number, these additives facilitate starting of the engine, which is of very great importance when the engine is operated during the winter.

The effects of additives depend on the chemical composition of the fuel: direct-distilled fuels are more sensitive to additives than fuels obtained by cracking [1]. Thus, for example, addition of 0.25% by volume of amyl nitrate* raises the cetane number of a direct-distilled fuel by 7 units, while that of a fuel obtained by catalytic cracking is raised only by 3 units [22]. This additive is stable and safe for storage, and is quite effective [4, 5].

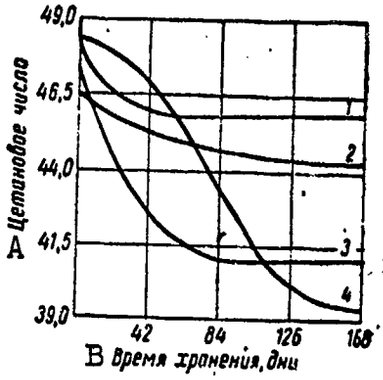



Fig. 115. Change in cetane number of fuel during storage after elevation of cetane number with additives [7]. 1) Diesel fuel with nitrocarbamide; 2) same fuel with peroxide additive; 3) same fuel with nitrates; 4) same fuel with nitroparaffins. A) Cetane number; B) storage time, days.

During storage of fuels with certain additives used to raise cetane number, a subsequent drop in cetane number was observed (Fig. 115), since additives of this type are active compounds and have inadequate chemical stability [3]. Consequently, not all effective additives are in commercial use.

For domestic diesel fuels, the use of additives to raise cetane number is not of great importance, since relatively small amounts of low-cetane fuels are produced.

However, addition of such additives (for example, alkyl nitrate) to winter-grade diesel fuels (with cetane numbers lower than 45-48) is recommended, particularly in view of their beneficial influence on engine starting.

Complete combustion of the fuel, stability of the flame with the engine operating under various conditions, and minimum scale formation is required for jet-engine fuels.

These combustion characteristics of the fuel depend chiefly on the design features of the engine, but they are determined to a considerable degree by fuel quality as well.

In recent years, broad-scale research has been under way to improve combustion of jet-engine fuels by use of additives to them.

Complete combustion of jet fuels and reduced scaling are achieved by addition of additives of the same type as used to improve combustion of diesel fuels. Thus, for example, combustion of a high-aromatic fuel was improved considerably by addition of organic peroxides [1]. Certain sulfur compounds have been proposed for this same purpose:

thiophenol pitch and tertiary butylthiophene [1].

Diethyl ether, propylene oxide and nitrobenzene, ethyl nitrate, and ethyl- and amyl nitrites in high concentrations (up to 5%) have been found effective in inhibiting self-ignition of kerosene [1].

Combustion catalysts are added to the fuel to improve combustion; these are chiefly organic compounds of metals – copper, iron, chromium, cobalt, nickel or manganese – that are soluble in the fuel [22]. The introduction of such additives into the fuel may also produce undesirable consequences – lowered chemical stability of the fuel, increased ash content, and so forth [22]. Most promising as additives for jet-engine fuels are those of the peroxide type and the alkyl nitrates.

Additives that Reduce Scaling in Engines

Scaling in an engine, which depends on fuel quality, can be reduced by the use of certain additives. "Antiscaling" additives are used basically with automobile ethylated gasolines and diesel fuels.

Compounds containing phosphorus or boron [6, 1]* have come into most widespread use as additives to ethylated automobile gasolines. These additives react with the lead compounds that form the basic part of the scale on combustion of ethylated gasoline, and form chemical compounds with lead that possess completely different properties.

For example, a compound of phosphorus with lead, $Pb_3(PO_4)_2$, remains nonconductive at high temperatures, while the conductivity of the lead-and-bromine that forms part of the scale ($Pb, Br_2$) [sic] drops sharply even at moderate temperatures. It is this that accounts for the improved operation of spark plugs when phosphorus additives are added to gasoline [8]. The practical effect of using such additives may be illustrated by the following examples. Addition of a phosphorus additive (tricresyl phosphate) to gasoline made it possible to more

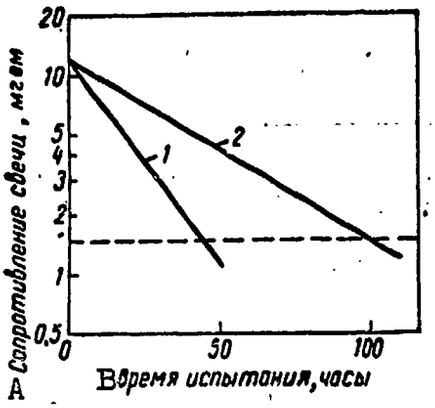



Fig. 116. Influence of phosphorus additive on change in spark-plug resistance as a function of test time [9]. 1) Ethylated gasoline without additive; 2) ethylated gasoline with tricresyl phosphate additive (plug works satisfactorily while its resistance remains above the level indicated by the broken line). A) Plug resistance, megohms; B) test time, hours.

than double the service lives of the plugs without short-circuiting of the electrodes (Fig. 116) [9].

When eight automobiles were road-tested, it was established that the mileage without fouling of spark plugs can be increased by 70 to 150% when phosphorus additives are used with the gasoline.

When an engine has been operated for a long time, its gasoline-octane-number requirements usually rise; when a gasoline with phosphorus additives is employed, this increase in octane requirement is negligible.

TABLE 73

Variation in Engine's Octane Requirement After Engine had Operated on Gasoline Without Additives and with Phosphorus Additive [40]

| 1 Автомобиль | 2 Требуемое октановое число топлива после работы на бензине | | 5 Снижение требуемого октанового числа |
|---|---|---|---|
| | 3 без присадки | 4 с фосфорной присадкой | |
| 1 | 90 | 88 | 2 |
| 2 | 90 | 86 | 4 |
| 3 | 92 | 86 | 6 |
| 4 | 94 | 90 | 4 |
| 5 | 94 | 86 | 8 |
| 6 | 96 | 88 | 8 |
| 7 | 96 | 96 | 0 |
| 8 | 94 | 92 | 2 |

1) Vehicle; 2) required fuel octane number after operation on gasoline; 3) without additive; 4) with phosphorus additive; 5) reduction of required octane number.

Road tests run with motor vehicles indicated that after an engine has operated on a gasoline containing phosphorus additives, it can run on a fuel with an octane number 2-8 units lower than after operation on a gasoline without additives (Table 73).

The ability of phosphorus additives to prevent premature self-ignition of the mixture is accounted for by the fact that the complex compounds of phosphorus and lead that formed produce almost no lowering of the ignition temperature of carbon, while the lead-bromine compounds (which form in the absence of additives) reduce it considerably [10].

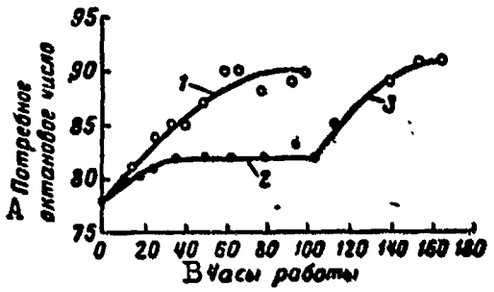



Fig. 117. Influence of boron-containing additives on required gasoline octane number [11]. 1) Without additive; 2) with butyl boron additive; 3) experiment continued without additive. A) Required octane number; B) hours of operation.

Thus, the self-ignition temperatures of the deposits are as follows:

carbon (carbon black)..... 500°

carbon and lead-bromine compounds..... 200-300°

carbon and lead-phosphorus compounds..... 350-470°

For this reason, the scales cannot act as self-ignition sources when phosphorus additives are used [10].

In road tests of an engine operating on a gasoline with a phosphorus additive, the number of cases of premature ignition was half

that observed in operation of the engine on a gasoline without additives.

The action of the boron-containing additives is accounted for in terms of suppression of the catalytic effect of the scale on the preflame processes. In the absence of TES, such additives are ineffective [1].

Research indicates that the addition of 0.04% of a boron-containing additive to gasoline is equivalent to increasing the TES concentration from 1.07 to 1.4 ml/kg. The effect of adding a alkyl-boron additive (butyl boron) may be seen from Fig. 117 [11]. When an alkyl-boron additive was used, cases of premature self-ignition were reduced by almost half and the total quantity of scale diminished.

A rather large number of different compounds have been studied as antiscaling additives; these include tributyl phosphite, trimethyl phosphite or phosphate, chloropropyl thiophosphate, cyclic phosphate, trialkyl phosphines, alkylaryl thiophosphates or thiophosphites, alkyl-boric acids or their esters, polyglycol esters of boric acid or esters of the lower alcohols, glycol borates, etc. [23].

Two additives that are produced under the trade names ICC (Ethyl Corporation) [12] and ICA (Shell) [8] have become the chief additives used commercially in the USA.

The ICC additive contains basically chloropropyl thiophosphate. It may be used in concentrations of 0.014% by volume with a TES content of 0.05% by volume in the gasoline.

The ICA additive – tricresyl phosphate $(CH_3C_6H_4O)_3PO_4$ – is an organic ester of phosphoric acid. In Germany, this additive is produced under the trade name TCP [8]. It is used in the same concentrations as the thiochlorophosphate additive.

A reduction in scaling in automobile engines is also achieved

the use of additives that improve completeness of fuel combustion. One compound suggested for this purpose is an alcoholate (isopropylate) of aluminum in concentrations from 0.01 to 0.1%.

It is assumed that on decomposition in the combustion zone, the additive forms aluminum oxide, which is mixed with the carbon and lead deposits and contributes to scavenging of the scale in the form of flakes [13].

Acetylacetone compounds of metals – triacetylacetone of iron and acetylacetone of cobalt – have also been tested successfully in automobile engines. The additives are added to the fuel in quantities from 0.03 to 0.04% (on the metal) [14].

Compounds that improve completeness of fuel combustion also contribute to reducing scaling in diesel engines if these scales are formed as a result of action of the fuel.

Scaling is promoted by the presence of considerable quantities of polyaromatic and unsaturated hydrocarbons in the fuel, as well as certain sulfur compounds. Scaling is reduced effectively when high-aromatic diesel fuels are employed by the addition of peroxide additives (e.g., isopropyl benzene hydroperoxide) [15].

One of the first diesel-fuel antiscaling additives – the additive dislip – contains manganese, barium, calcium and phosphorus compounds that are soluble in the fuel. The manganese salts serve as combustion catalysts and reduce the quantity of scale; the phosphorus and alkali-metal compounds reduce corrosion and scaling caused by the sulfur oxides; the phosphorus compounds modify the scale. Lanolin derivatives are added to the additive to improve its lubricating and protective properties. The basic components of the additive dissolve in nonvolatile aromatic solvent.

Tests have shown that when a diesel fuel is used with the dislip

additive, the quantity of scale on the nozzles was reduced and the condition of the valves improved [16].

The amounts of scale and smoke formed were also reduced when acetylacetone compounds of metals (iron, cobalt) were used as additives; these were added to diesel fuel in quantities from 0.03 to 0.04% (on the metal) [14].

Increased scaling when high-sulfur diesel fuels are used is one of the most serious operational difficulties, and one that can be eliminated to a considerable degree by the use of special fuel additives (see page 434).

## ADDITIVES THAT IMPROVE CHEMICAL STABILITY OF FUELS UNDER OPERATIONAL CONDITIONS

Additives of this type are most widely employed in fuel applications. Additives that improve the chemical stability of fuels under operating conditions include substances added to the fuel to inhibit the oxidation processes that take place under conditions of prolonged storage and in the engine's fuel system, to suppress the catalytic action of active metals, which accelerate these processes, to disperse insoluble oxidation products and prevent formation of these products in the fuel; they also include compounds that perform several functions.

### Inhibition of Fuel Oxidation Under Conditions of Storage and in Engine Fuel System

Chemical changes caused by oxidation of unstable components take place in the fuels during transportation, pumping and prolonged storage. Although these changes exert only a secondary influence on the actual motor properties of the fuels -- their heats of combustion, octane or cetane numbers -- they may sharply reduce the usefulness of the fuel in an engine, since the oxidation products interfere with normal operation of the fuel system. In fuels that are by nature particul..

unstable chemically, the consequences of oxidative processes are even more serious, and such fuels cannot be used without chemical stabilization.

Antioxidants are added to fuels to inhibit oxidation processes [1]. They are introduced into the fuel in hundredths or thousandths of a percent. The antioxidants break the chains of oxidation reactions in the fuel. They may react with hydrocarbon or active peroxide radicals, as well as hydroperoxides, with formation of nonactive radicals that are incapable of perpetuating the oxidation-reaction chain. In contributing to conversion of the active compounds into stable states, they prevent the development of chains and slow down the entire oxidation process.

The development of oxidation processes in a fuel containing an antioxidant takes place only after the additive has been exhausted.

Depending on the chemical composition of the fuel and the conditions under which it is used, a given antioxidant may show varying effectiveness, since the relative activity of the interacting radicals may change [17]. For example, certain antioxidants that provide good stabilization for unsaturated fuels are ineffective in direct-distillation gasolines containing tetraethyl lead. Certain antioxidants that stabilize gasolines are unsuitable for kerosenes and diesel fuels [18]; additives that retard oxidation of fuels at storage temperatures are not effective at elevated temperatures in the fuel system of an engine [19].

A large number of substances belonging to various chemical classes have been studied as potential antioxidants; many active compounds have been found, particularly among the phenols, aminophenols, alkyl phenols and alkylaminophenols, as well as among certain sulfur-containing substances [1]. At the present time, specific compounds and tech-

nical products (Table 74) have come into use for fuels of various types in domestic and foreign fuel-stabilization practice.

Alkyl phenols (Table 74) are general-purpose antioxidants suitable for fuels of all types. They are quite soluble in fuels, stable in hydrocarbon media at various temperatures, and practically insoluble in water. The only shortcoming of these antioxidants is the high concentration required in the fuel.

Aminophenols (Table 74). N-n-butyl-p-aminophenol is particularly recommended in the USA for unsaturated fuels, but is also permitted by the standards for ethylated aviation gasolines and jet fuels; it is produced in alcohol solution (50-52% of solvent). It is not used in domestic practice for stabilization of fuels.

Phenyl-p-aminophenol is an extremely good domestic antioxidant for ethylated aviation gasolines, and one that is effective in very low concentrations; it is also recommended for automobile gasolines (but higher concentrations are required for them) and jet fuels. Its shortcoming is solubility in water at elevated temperatures and poor solubility in fuels with higher molecular weights.

Amines (Table 74). Derivative of p-phenylenediamine; recommended for fuels containing cracking products, but permitted by USA standards for aviation gasolines and jet fuels. The deficiencies of the antioxidant are its toxicity and instability in storage. It is not used in domestic practice.

Polyphenols (Table 74). Antioxidants of this type are used on a limited scale; they are not suitable for stabilization of ethylated direct-distilled fuels. The commercial antioxidants are technical products in which the content of active component is sometimes less than 50%. For this reason, and also as a result of their relatively low effectiveness, they are used in considerably higher concentrations than

the individual compounds examined above.

Wood tar distillates were some of the first commercial antioxidants and are in use to this day for stabilization of automobile gasolines and tractor kerosenes. Ordinary antioxidant types are less effective in kerosenes. Improved wood tar additives ("pyrolyzate inhibitor preparation") are also satisfactory in kerosenes, including aviation kerosenes.

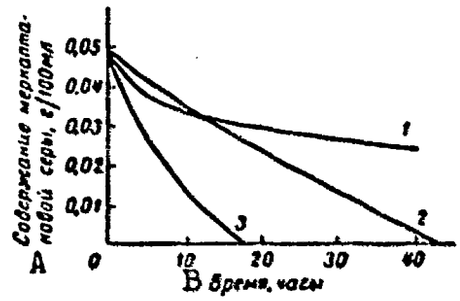



Fig. 118. Influence of hydrocarbons on mercaptan oxidation rate in presence of antioxidant (butyl mercaptan) [21]. 1) Saturated; 2) alkylaromatic; 3) olefins. A) Mercaptan-sulfur content, g/100 ml; B) time, hours.

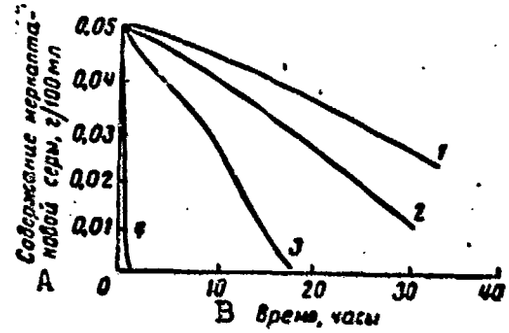



Fig. 119. Influence of mercaptan structure on rate of their oxidation in the presence of antioxidant (in olefinic hydrocarbons) [21]. 1) Tertiary; 2) secondary; 3) primary; 4) aromatic. A) Mercaptan-sulfur content, g/100 ml; B) time, hours.

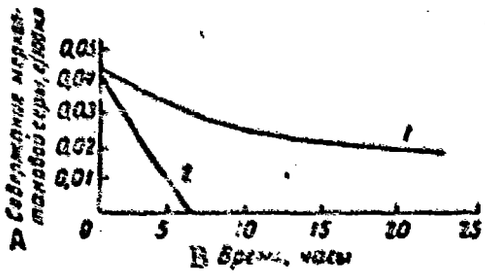



Fig. 120. Influence of antioxidant on oxidation rate of butyl mercaptan in olefins [21]. 1) Without antioxidant; 2) with antioxidant. A) Mercaptan-sulfur content, g/100 ml; B) time, hours.

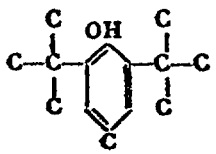
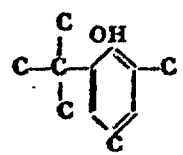
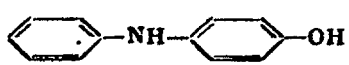
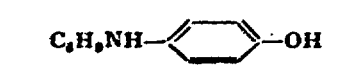
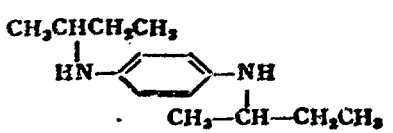
Antioxidants based on coal-tar polyphenols (FCh-16, FCh-4) are considerably more effective.

A shortcoming of these antioxidants (as for the amines and aminophenols) is their limited solubility in fuels, and particularly in the high-molecular-weight fractions (kerosenes, diesel fuels).

Antioxidants are added to the fuel at the refineries directly during production, before oxidation products have had time to accumulate

TABLE 74

Commercial Antioxidants Used to Stabilize Various Types of Fuels [1, 20, 24]

| 1 Антиокислители | 2 Химическая формула активного компонента | 3 Примерные концентрации, % вес. | 4 Физические свойства: 5 внешний вид | 6 плотность, г/см³ | 7 температура, °С: кипения | плавления | вспышки | 11 мол. вес активного компонента | 12 Область применения |
|---|---|---|---|---|---|---|---|---|---|
| **13 Алкилфенолы** | | | | | | | | | |
| 14 2,6-ди-*трет* бутил-4-метил-*п*-фенол (ионол, топанол О, дюпон 29) |  | 0,03—0,004 | 15 Белые или светло-желтые кристаллы | 1,04 | 260 | 69 | 127 | 220,4 | Автомобильные бензины, авиационные бензины, реактивные топлива 16 |
| 17 2,4-диметил-6-*трет*-бутил-*п*-фенол (топанол А) |  | 0,03—0,004 | 18 Бледно-желтая жидкость | 0,961 | 246—252 | — | 110 | 178,2 | То же 19 |
| **20 Аминофенолы** | | | | | | | | | |
| 21 Фенил-*п*-аминофенол (*п*-окси-дифениламин) |  | 0,004—0,008 | 22 Светло-серый порошок | — | 330 | 70 | — | 185,2 | Авиационные бензины, автомобильные бензины 23 |
| 24 N-*н*-бутил-*п*-аминофенол (UOP 4*), дюпон 5, тенамен 1) |  | 0,002—0,005 | 25 Жидкость | 0,90 | — | —30 | 16 | 165,2 | Главным образом бензины, авиационные топлива 26 |
| **27 Амины** | | | | | | | | | |
| 28 NN'-ди-*втор*-бутил-*п*-фенилендиамин (UOP 5, дюпон 22, тенамен 2, топанол М) |  | 0,002—0,004 | 29 Красная жидкость | 0,95 | 295—300 | 15 | 146 | 220,3 | Рекомендован для авиационных керосинов; главным образом для топлив, содержащих продукты крекинга; для облагораживания сернистых бензинов; авиационные бензины 30 |
| **31 Полифенолы** | | | | | | | | | |
| 32 Фенолы из угольной смолы ФЧ-16, ФЧ-4 | 33 Смесь полифенолов | 0,05—0,1 | 34 Темно-коричневая жидкость | 1,15 | 35 до 220 40%, до 270 90% | — | — | — | Автомобильные бензины, тракторные керосины; рекомендован для авиационных керосинов 36 |
| 37 Фенолы из древесной смолы (древесносмольный антиокислитель Б, UOP-1) | 38 Смесь полифенолов и их эфиров | 0,05—0,1 | 39 То же | 1 | 230—310 | — | — | — | Автомобильные бензины, тракторные керосины 40 |

*Contains 50% of solvent: anhydrous methyl alcohol or isopropanol.

KEY TO TABLE 74

1) Antioxidant; 2) chemical formula of active component; 3) typical concentrations, % by weight; 4) physical properties; 5) external appearance; 6) density, $g/cm^3$; 7) temperature, °C; 8) boiling; 9) melting; 10) flash; 11) molecular weight of active component; 12) range of application; 13) alkyl phenols; 14) 2,6-di-tert-butyl-4-methyl-p-phenol (ionol, topanol O, DuPont 29); 15) white or light yellow crystals; 16) automotive gasolines, aviation gasolines, jet fuels; 17) 2,4-dimethyl-6-tert-butyl-p-phenol (topanol A); 18) pale yellow liquid; 19) same; 20) aminophenols; 21) phenyl-p-aminophenol (p-hydroxydiphenylamine); 22) light gray powder; 23) aviation gasolines, automobile gasolines; 24) N-n-butyl-p-aminophenol (UOP 4*), DuPont 5, tenamen 1); 25) liquid; 26) chiefly gasolines and aviation fuels; 27) amines; 28) NN'-di-sec-butyl-p-phenylenediamine (UOP 5, DuPont 22, tenamen 2, topanol M); 29) red liquid; 30) recommended for aviation kerosenes; chiefly for fuels containing cracking products; for improvement of sulfur-containing gasolines; aviation gasolines; 31) polyphenols; 32) phenols from coal tar: FCh-16, FCh-4; 33) mixture of polyphenols; 34) dark brown liquid; 35) 40% below 220, 90% above 270; 36) automotive gasolines, tractor kerosenes; recommended for aviation kerosenes; 37) phenols from wood tar (wood tar antioxidant B, UOP-1); 38) mixture of polyphenols and their ethers; 39) same; 40) automobile gasolines, tractor kerosenes.

in it. When this is done, the effect of the antioxidant is maximal, since the additive is not consumed unproductively in reactions with oxidation products that have already formed from the fuel. The period of effectiveness of an antioxidant introduced into a fuel may be prolonged by addition of new doses of antioxidant during storage of the fuel, in the stage when the initial dose of antioxidant has not yet been fully exhausted [1]. The addition of antioxidant in fuel storage may be effected by continuous injection of small quantities of antioxidant (a slowly soluble substance is placed in the layer of fuel) or by periodic injection of the entire prescribed dose [1].

A special region of application of certain antioxidants is their use to improve gasolines containing mercaptans ("sweetening") [21].

It has been found in recent years that the antioxidant NN'-di-sec-butyl-p-phenylenediamine accelerates oxidation of mercaptans to disulfides and sulfides at moderate temperatures. Here the antioxidant takes the role of a catalyst and is not itself used up, so that it is

not necessary to introduce additional antioxidant to guarantee chemical stability of the gasoline.

Sulfur-containing gasolines are improved by the use of antioxidant at temperatures from 20 to 45°, depending on the type of gasoline. The gasoline is first washed with alkali (in one or two stages) and then dosed with the NN'-di-sec-butyl-p-phenylenediamine, after which air is passed through. Sometimes the air dissolved in the gasoline is sufficient to oxidize the mercaptans, and it is not necessary to supply additional air. The process is completed by the time the gasoline has passed through the factory tanks (approximately one day).

In the presence of unsaturated hydrocarbons, the mercaptans oxidize more readily (Fig. 118), so that thermal-cracking and catalytic-cracking gasolines are sweetened better by the antioxidant than are direct-distilled gasolines.

The rate of oxidation depends on the type of mercaptans (Fig. 119); aromatic mercaptans oxidize most easily.

The catalytic action of the antioxidant may be seen in the example furnished by the oxidation of n-butyl mercaptan in olefins (Fig. 120).

Apart from the above factors, the rate of the process depends on the mercaptan concentration, the molecular weight of the mercaptans, and the temperature of the process.

The process is run successfully at normal concentrations of the antioxidant required for chemical stabilization; an increase in concentration does not produce an additional effect.

Only antioxidants of this type are used to sweeten gasolines containing mercaptans. Aminophenol antioxidants, on the other hand, inhibit mercaptan oxidation [21]. Moreover, they are extracted by alkali.

In the USA, sulfur-containing gasolines are successfully sweet[illegible]

with antioxidants at a number of petroleum refineries instead of using doctor purification [21].

The use of existing commercial antioxidants in fuels guarantees that they will retain their properties under ordinary conditions for prolonged periods (1-3 years) and permit subsequent normal use in engines. However, prolonged storage of a fuel in hot climates or normal use of the fuel under comparatively severe conditions – elevated temperatures, in the presence of nonferrous metals – is not always ensured by antioxidants alone.

The same applies to high-molecular fuels such as diesel fuels that contain large amounts of unsaturated hydrocarbons and sulfur compounds.

In these cases, the use of antioxidants alone is inadequate and chemical stabilization of the fuels requires use of additives of other types as well.

Suppression of Catalytic Action of Metals Under Conditions of Fuel Storage and in Engine Fuel Systems

Metals present in the oxidation zone in the form of metallic surfaces, soluble salts, and so forth, accelerate oxidation of fuels. A very small quantity of metal is sufficient for its catalytic action to be manifested, since catalysis is effected by ions of the metal [25-27]. Copper, copper alloys and certain other metals (vanadium and sometimes lead) possess the highest catalytic activities [25, 28, 1]. In the presence of an antioxidant, the influence of the metal comes particularly strongly to the fore; the antioxidant is consumed rapidly and the fuel, left unprotected, begins to oxidize [27, 29].

In practical application of the fuels, the catalytic action of metallic surfaces composed of active metals results in considerable operational difficulties. Tar deposits form on nonferrous-metal compo-

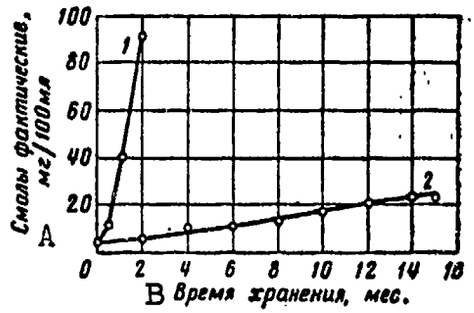



Fig. 121. Influence of metal deactivator in stabilizing automobile gasoline during storage [29]. 1) Gasoline stabilized by antioxidant only; 2) gasoline stabilized by antioxidant and metal deactivator. A) Actual tars, mg/100 ml; B) storage time, months.

nents (pickup tubes, filter screens, plungers) in the fuel systems of engines (automobile, jet and diesel types) and lower the dependability and economy of the engine. Traces of metals, including active metals, are present in practically all fuels. It was established by investigation of 240 gasoline specimens (from the columns) that, for example, 91% of them contained 0.9 mg/liter of copper [28]; this is quite sufficient for full

TABLE 75

Effectiveness of Metal Deactivators in the Presence of Various Antioxidants [1]

| 1 Антиокислитель | 2 Смолы, мг/100 мл в крекинг-керосине* | | | |
|---|---|---|---|---|
| | 3 без металла | 4 в присутствии меди | 5 с медью и с добавлением деактиватора | |
| | | | 6 салицилиден-о-аминофенола 0,013% | 7 дисалицилиденэтилендиамина 0,02% |
| 8 Ионол 0,2% вес. | 24 | 68 | 36 | 26 |
| 9 Фенил-л-аминофенол 0,2% | 24 | 129 | 26 | 18 |
| 10 ФЧ-16,1% | 21 | 32 | 19 | — |
| 11 ФЧ-4,1% | 24 | 64 | 19 | 28 |
| 12 Древесносмольный марка ТП 0,1% | 19 | 87 | 21 | — |
| 13 Древесносмольный сорта Б 0,1% | 11 | 212 | 50 | — |

*After oxidation for 4 hours at 100°.

1) Antioxidant; 2) tars, mg/100 ml in cracking kerosene*; 3) without metal; 4) in presence of copper; 5) with copper and deactivator; 6) 0.013% salicylidene-o-aminophenol; 7) 0.02% disalicylidene-o-aminophenol; 8) ionol, 0.2% by weight; 9) phenyl-p-aminophenol, 0.2%; 10) FCh-16.1% [sic]; 11) FCh-4.1% [sic]; 12) wood tar antioxidant, type TP, 0.1%; 13) wood tar antioxidant, type B, 0.1%.

manifestation of its catalytic action.

Special additives – metal deactivators – are added to fuels to

suppress the catalytic action of metals. These additives are used together with antioxidants to protect the latter from attack by metals [25-29]. Metal deactivators are added in concentrations 1/5 to 1/10 those of the antioxidants.

The action of these additives is based on their formation, with the metallic ions, of complexes that are soluble in the fuel and convert the metals to inactive states [25-27]. For this reason, substances capable of forming complexes of definite structure with metals are used as metal deactivators [26, 27]. Compounds of the most diverse chemical classes are effective for this purpose.

The largest number of active metal deactivators is found among compounds of the Schiff-base type (condensation products formed by hydroxyaromatic carbonyl compounds with amines, amino alcohols, aminophenols, etc.) and, in particular, the salicylidenes, which are condensation products of salicylal with amines or aminophenols [25-29].

Among the salicylidenes described as effective metal deactivators, we note salicylidene-o-aminophenol, disalicylideneethylene diamine, and tetrasalicylidene-tetra(aminomethyl)methane [25-29, 1].

The metals deactivators do not themselves possess antioxidant properties, but on addition to a fuel containing an antioxidant, they intensify its action considerably (Table 75).

Metals deactivators were first intended for stabilization of sulfur-containing gasolines that had been purified with copper salts, since the traces of copper that remain in the gasoline cause a sharp deterioration in its stability [25]. Subsequently, they came into use in practically all fuels. Figures 121 and 122 illustrate the effectiveness of a metal deactivator in stabilizing automobile gasoline and aviation kerosene containing unsaturated hydrocarbons [1, 29].

Comparatively extensive commercial use as a metals deactivator

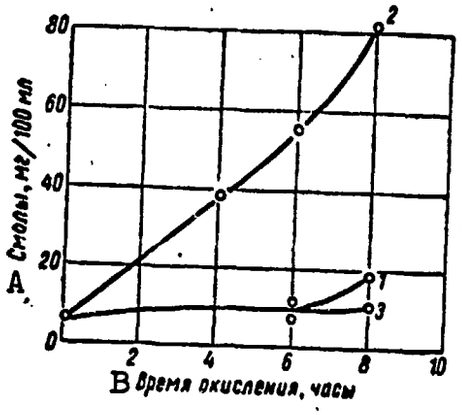
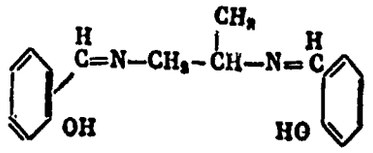



Fig. 122. Influence of metal deactivator in stabilizing gasoline-kerosene fractions [1]. (Oxidation at 110° in an atmosphere of air in the presence of copper in the form of platelets.) 1) Oxidation in absence of copper, fuel without additive; 2) oxidation in presence of copper, fuel without additive; 3) oxidation in the presence of copper with metal deactivator added to fuel. A) Tars, mg/100 ml; B) oxidation time, hours.

has been accorded abroad to disalicylidenepropylenediamine or NN'-disalicyl-1,2-propanediamine:




In pure form, this is a dark amber liquid with a specific gravity of about 1.08 and a pour point of −18° [28].

The metals deactivator is shipped in a solvent – toluene or xylene – which makes up 20% of the additive. The additive is sold under various trade names – DMD, tetramen-60 [28].

Specifications provide for the addition of 0.005% by weight of the metal deactivator to automobile gasolines and jet fuels [28, 22]. It is added to kerosene to improve color [28].

In addition, metal deactivator is used in certain complex additives – FOA-208 and FOA-212, which are produced for stabilization of diesel and boiler fuels [22]. In these additives, the metal deactivator composes 8 and 12%, respectively, but the basic component is the FOA-2 dispersing additive (see below).

Prevention of Sludge Formation in Engine's Intake System

In an engine's fuel system (in the intake system), sludge deposits form from tarry substances, nonvolatile products (dyes) and foreign impurities.

To ensure cleanliness of the fuel system, special gasoline additives have been proposed; these either dissolve the deposits or pre-

vent adhesion of the deposits to the metal by virtue of their surface-active properties. Below we list certain compounds that have been proposed as additives that wash sludge deposits out of automobile-engine fuel systems: polymerized esters of unsaturated acids or copolymers with vinyl acetate, amyl fumarate or maleate, silicones, silicones with aryl phosphate, isopropane, etc. [23].

Additives of the neutral-oil type ensure the presence of liquid on the walls of the apparatus and thus keep the deposits in the suspended state, assisting in scavenging them out. Simultaneously, they provide further lubrication for the intake valves, cylinder walls, and piston rings. Such additives are added to gasoline in a concentration of 0.5%.

Surface-active additives are used in concentrations from 3-4 mg/100 ml.

Additives that clean the fuel system are not added to aviation gasolines [23].

Improvement of Fuel Properties with Detergent Stabilizers

The chemical changes that take place in fuels under the conditions of storage and in the engine's fuel system are accompanied by formation of both fuel-soluble and fuel-insoluble oxidation products.

Insoluble deposits are formed when jet and particularly diesel and boiler fuels containing cracking components are stored [30-34, 22].

The formation of deposits in direct-distilled jet fuels at high temperature is a special problem; it is considered in Chapter 10.

Elimination of deposit formation in storage of diesel fuels becomes an important operational problem, particularly when products of catalytic cracking are used extensively in these fuels [30-37].

We note two types of deposits: sludges, which represent an emulsion of organic oxidation products in water, and gelatinous mercaptan

deposits, which consist of fuel that has been contaminated by small quantities of copper mercaptides. The latter form when a sulfur-containing fuel acts on copper alloys, from which fuel-apparatus components are made.

A fuel containing insoluble deposits cannot be used normally because of clogging of the filters, screens and clearances in the engine nozzles [30-34].

Special additives are used successfully to improve the operational properties of fuels that are inclined to form deposits; these are the detergent stabilizers. These additives perform several functions: they prevent formation of deposits during storage by retarding oxidation processes and prevent the insoluble products that have formed from precipitating by holding them in a fine-dispersed state. A mixture of additives in which these functions are performed separately by two (or three) additives may be employed.

Dispersing agents apparently have their effect as a result of their surface-active properties as classical stabilizers (peptizers) of colloidal systems, preventing coagulation of colloidal particles of insoluble oxidation products from the fuel.

When the additive concentration in the fuel is inadequate, an increase in the quantity of deposit was sometimes observed. This phenomenon is accounted for by the fact that in fuels in which the colloidal concentration is higher than the additive concentration, the latter may precipitate from solution together with these substances, while with adequate concentrations it peptizes them successfully [34]. The inhibiting effect of the additives is realized by the normal antioxidant mechanism.

A large number of compounds have been suggested as additives to diesel and boiler fuels for use in preventing formation of deposits

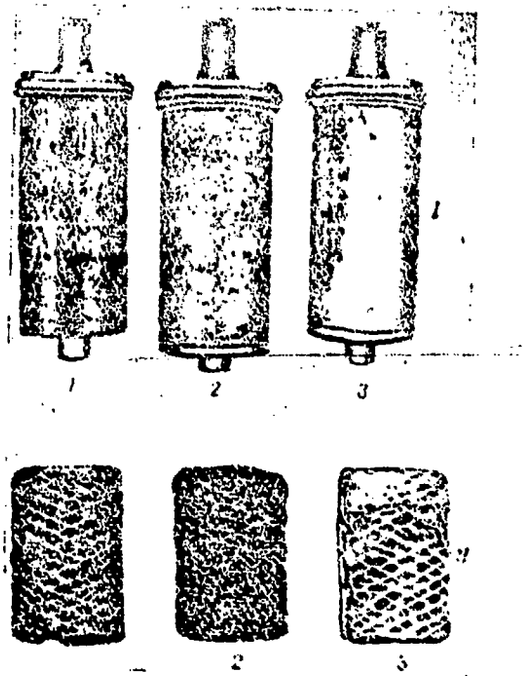


Fig. 123. Influence of detergent additives to fuel on cleanliness of filters [33, 34]. I) Pump filters after 16 weeks of operation at 60°; 1) gas oil without additive; 2) same gas oil with 0.025% of No. 2 additive; 3) same gas oil with 0.025% of No. 1 additive. II) Filters from boiler installations: 1) fuel without additive; 2) fuel with commercial additive; 3) fuel with experimental additive.

them; these belong chiefly to the classes of alkylamines, sulfonates, naphthenates and phenolates of the alkaline-earth metals, phosphorus compounds, fatty acids, and polar polymers containing nitrogen bases [1, 22, 28, 35, 30]. Metals deactivators are also sometimes added to such additives. These additives are classified as ashforming and non-ashforming in accordance with their composition. The former group includes compounds containing metals (naphthenates, sulfonates, phenolates of metals), while the second includes amines, polar polymers, and other purely organic substances. Such additives are used not only to prevent formation of deposits, but also to clean apparatus that has

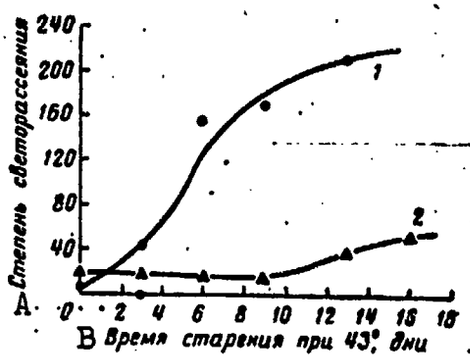



Fig. 124. Effectiveness of dispersing stabilizers in storage of diesel fuels [32]. (Based on light-dispersion changes by insoluble particles formed.) 1) Fuel without additive; 2) fuel with 0.02% of additive. A) Dispersion of light; B) aging time at 43°, days.

already been contaminated. In the latter case, the additive concentration in the fuel is increased [36, 37].

The activity of good dispersing or multifunctional additives is expressed in an improvement in the filterability of the fuel after storage and in greater cleanliness of the fuel-handling apparatus (Fig. 123).

The inhibiting action of complex additives (detergent stabilizers) manifests itself even in the very first

TABLE 76

Influence of Various Types of Commercial Additives on Formation of Insoluble Deposit in Fuel During Storage [31]

| 1 Присадки | 2 Нерастворимый осадок в топливе (в мг/100 мл) после хранения при 43° | |
|---|---|---|
| | 3 6 недель | 4 18 недель |
| 5 Без присадки . . . . . | 5.8 | 15.0 |
| 6 Алкиламин . . . . . | 2.4 | 9.0 |
| 7 Сульфонат металла . . . | 0.6 | 7.6 |
| 8 Полярный полимер . . . | 1.1 | 5.3 |

1) Additive; 2) insoluble deposit in fuel (in mg/100 ml) after storage at 43°; 3) 6 weeks; 4) 18 weeks; 5) without additive; 6) alkylamine; 7) metal sulfonate; 8) polar polymer.

stages of fuel storage (Fig. 124).

Although deposits do form in fuels during storage even when they have effective additives, the concentration by weight of these deposits is considerably lower (Table 76) and the structure of the deposit is modified, since it does not cause clogging of filters [31].

It has been noted that not all active cleansing additives that give a good account of themselves in oils are sufficiently effective in diesel and boiler fuels.

TABLE 77

Suspending Action of Certain Dispersing Agents in the Presence and Absence of Moisture [36]

| 1 Присадки | 2 Количество суспендированной сажи после четырех дней, % | |
|---|---|---|
| | 3 сухой керосин | керосин с 0,5% воды 4 |
| 5 Без присадки | 50 | 50 |
| 6 Сульфонат Ba 0,5% | 100 | 45 |
| 7 Полярный полимер 0,5% | 100 | 100 |

1) Additive; 2) quantity of suspended carbon after four days, %; 3) dry kerosene; 4) kerosene with 0.5% of water; 5) without additive; 6) Ba sulfonate, 0.5%; 7) polar polymer, 0.5%.

TABLE 78

Effectiveness of Polar Polymer in Reducing Quantity of Deposit on Nozzle Screens [36]

| 1 Топливо | 2 Концентрация присадки, % вес. | 3 Условия «старения» | | 6 Нерастворимый осадок, мг |
|---|---|---|---|---|
| | | 4 продолжительность, месяцы | 5 температура, °С | |
| 7 Легкий газойль каталитического крекинга с содержанием серы 0,9% вес. | 8 Без присадки | 6 | 43 | 177 |
| 9 То же | 0,05 | 6 | 43 | 9 |
| 10 То же топливо, содержавшее серы 0,37% вес. | 8 Без присадки | 9 | 11 Комнатная | 222 |
| 9 То же | 0,05 | 9 | » | 25 |

1) Fuel; 2) additive concentration, % by weight; 3) "aging" conditions; 4) time, months; 5) temperature, °C; 6) insoluble deposit, mg; 7) light catalytic-cracking gas oil with sulfur content of 0.9% by weight; 8) without additive; 9) same; 10) same fuel containing 0.37% by weight of sulfur; 11) room.

This is accounted for by the different conditions of application:

fuel additives must show their influence at considerably lower temperatures, at which condensation of moisture is possible, and this may "poison" the additive [36].

Table 77 shows the influence of water on the suspending action of certain additives with respect to insoluble products.

As will be seen from Table 6, the most effective dispersing agents are additives of the polar polymer type. These compounds are products of joint polymerization of two different types of monomers that perform different functions in the additive [36]. One of the monomers, which is nonpolar in nature, ensures solubility of the additive in the fuel, acting as an olecphilic component. The other monomer contains nitrogen bases and is the active component of the additive. On the whole, such additives may be characterized as hydrocarbon-soluble surface-active polymers containing nitrogen bases [36].

To a considerable degree, the properties of an additive depend on the contents in it of the components that perform the functions indicated above.

Still another nonpolar monomer, which functions only to elongate the polymer chain, may also be incorporated in the additive [36].

Compounds of the following classes may be employed as monomers with various functions to produce polar copolymers: esters or amides of methacrylic or acrylic acids or polymerizing polycarboxylic acids, vinyl esters of carboxylic acids, and so forth.

High surface-active (suspending and dissolving) properties are ensured in such additives by the presence of $NH_2$ groups in them. Neutralization of these basic groups does not reduce the suspending properties [36].

A copolymer of dodecyl methacrylate and diethylamine ethyl methacrylate in the proportions 80:20 has been found most effective as a

stabilizer-detergent for diesel and boiler fuels [36, 35].

Table 78 indicates the influence of this additive on the filterability of fuel after aging [36].

A typical additive among the class of polar polymers is the type FOA-2 additive (Fuel Oil Additive, No. 2 – an additive to boiler fuel No. 2).

The additive is delivered in solvent kerosene; the active component – the polar polymer – composes 50% of it. The polymer incorporates molecules of various sizes; the average molecular weight of the polymer is about 50,000 [35]. Certain physical properties of the FOA-2 additive are listed below.

| | |
|---|---|
| Density, $g/cm^3$ | 0.902 |
| Flash point, °C | 41 |
| Pour point, °C | –29 |
| Alkali equivalent, mg of KOH/g | 13.8 |
| Solubility in water, % by weight | less than 0.01 |
| Viscosity at 100°, cst | 65 |

The additive is stable at various operating temperatures, either in the fuel or in pure form. Decomposition of the additive's active component intervenes only at temperatures above 425° [35].

The additive is added to diesel, distillate and residual boiler fuels in concentrations ranging from 2 to 17 mg/100 ml; the most common concentration is 4–8 mg/100 ml [35].

To increase the effectiveness of the additive and prevent formation of gelatinous mercaptan deposits in sulfur-containing fuels, 8–12% of DND metals deactivator is added to it (FOA-208 and FOA-212) [35].

The presence of an active detergent-stabilizer in the fuel fully solves the operational problem of preventing formation of deposits in diesel fuels that contain cracking products.

In addition, dispersing additives also facilitate mixing of fuels. When diesel and boiler fuels of different origins (and different viscosities) are mixed, we frequently observe precipitation of deposits as a result of changes in the properties of the solvent medium [37].

When detergents are present in the fuel, these difficulties do not arise. This advantageous property of additives is particularly important for railroad and marine transportation, which are obliged to use fuels obtained at various geographical points.

The fuel additives described above are, as a rule, multifunctional: antioxidants, dispersing agents, and sometimes corrosion preventives (polar polymers).

This does not exclude the use, when necessary, of such additives in mixtures with others to bolster one or another function, such as the anticorrosive or antioxidant properties.

ADDITIVES THAT REDUCE CORROSIVE ACTIVITY OF FUELS

Fuel hydrocarbons are, in themselves, substances that are not aggressive toward metals, but the oxygen and sulfur compounds that accompany them in the fuels and the halogens in the antiknock compounds may, under certain conditions, cause considerable corrosion of metals. This property comes particularly to the fore in the presence of water.

Reduction of the corrosive activity of high-sulfur fuels, the production of which is increasing continuously, is of great importance.

The corrosive properties of fuels may be reduced to a considerable degree by the use of various additives.

Reduction of Corrosion Due to Fuel-Oxidation Products

As oxidation products – chiefly organic acids – accumulate during storage of fuels, the corrosive aggressiveness of the fuels increases.

Additives may inhibit this intensification of corrosive activity of fuels either by retarding oxidation of the fuels or by forming a

protective film on the metal.

Oxidation is retarded by the usual antioxidant method; a protective film may be created either as a result of chemical reaction between the additive and the metal or as a result of formation of a monomolecular layer (barrier) due to oriented adsorption of the polar substances [38].

Beyond this, certain compounds may retard corrosion by neutralizing acid oxidation products.

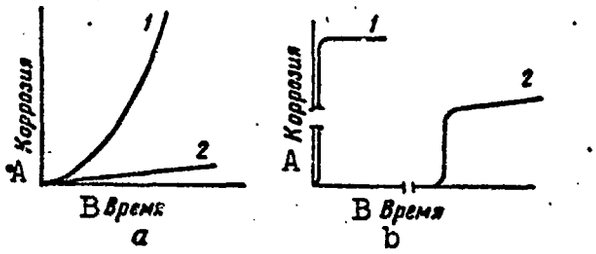



Fig. 125. Kinetic corrosion curves in the presence of various types of anticorrosion additives [39]. a) Inhibitor; b) immunizer. 1) Without additive; 2) with additive. A) Corrosion; B) time.

Anticorrosion agents are classified as immunizers, inhibitors and passivators in accordance with the kinetic mechanism by which they act [39].

The immunizers include substances addition of which to hydrocarbons prolongs the induction period prior to the onset of intensive corrosion; the inhibitors include additives addition of which lowers the rate of corrosion, without any induction period coming into evidence, and the passivators are compounds that prevent corrosion at the very outset by forming a protective film of corrosion products on the metal surface (Fig. 125).

Oxidation inhibiting by antioxidants and metals deactivators was discussed above. Stabilizing the fuel against oxidation, these addi-

tives also perform the functions of substances that reduce corrosion.

The actual anticorrosion additives are, however, certain compounds of a polar nature or neutralizing substances. These include long-chain fatty acids, esters, diesters, salts of fatty and naphthenic acids, hydroxycarboxylic acids, amines and other such compounds [40, 1, 22, 23].

The addition to direct-distilled kerosene (T-1) of small quantities (0.05-1%) of certain thiochloro- and amino-derivatives of hydrocarbons of the aliphatic and aromatic series reduced corrosion (of carbon and low-alloy steels and magnesium) to a fraction [40].

Sulfonated stearic acid, chlorinated paraffin, chlorinated rubber, diphenylamine and other substances have been tested as such additives. Some of these compounds protected steel from corrosion for over 1 year or even prevented it completely [40].

Corrosion by oxidation products is intensified particularly in the presence of water (dissolved in the hydrocarbons or present in the form of a separate phase), since the part taken by electrochemical corrosion increases in this case. Acid oxidation products concentrate in the aqueous phase as a result of their higher solubility in water, and corrosion is sharply intensified. During storage of ethylated gasolines in the presence of moisture, corrosion is aggravated as a result of hydrolysis of the halogen carrier [41, 42].

Corrosion of metals by ethylated gasoline was prevented by addition of sodium methoxydisulfamidoacetate $CH_3(CH_2)_{11-17}SO_2NHCH_3COONa$ to it (0.05-0.1% by weight). The additive forms a protective film that is easily restored on damage on the surface of the metal [42].

The use of alkali-metal (sodium, potassium) and ammonium fluorides, which are placed in the gasoline in cartridge form, also gave positive results in ethylated gasoline [42].

Aminoalkyl phosphates have also come into use as neutralizing anticorrosion gasoline additives. They are products of the reaction between aliphatic blanched amines ($C_4 - C_{15}$) and alkyl phosphates ($C_8 - C_{16}$) and contain about 50% excess amine as against the theoretical quantity. It is recommended that the additives be present in aviation gasolines in quantities from 0.002-0.05% [43]. Certain imidazoles may be used in such an additive instead of the aliphatic amines [43].

Basically, corrosion by fuel oxidation products formed during storage can be, for all practical purposes, prevented in the absence of moisture by oxidation-stabilizing additives alone; in the presence of water, however, the presence of such additives is inadequate and special additives are sought that will, in one way or another, protect the metal of the apparatus from attack by aggressive compounds in the fuel.

In the presence of water and air that is dissolved in the fuel, the usual rusting of metals also takes place, and rust inhibitors are used to prevent it.

A number of compounds such as, for example, salts of mepazin [sic] sulfamidoacetic acids, n-dihydroxybenzophenone, the monoethyl ether of ethylene glycol, N-acylamino acids, naphthenates, sorbitan esters and pentaerythritol esters, amino- and ammonium sulfonates (mahogany-colored sulfoacids) and others have been suggested as additives to prevent corrosion of the apparatus by fuels in the presence of water [40, 22].

For example, a mixture of alkylmercaptoacetic acid and the acid esters of monolaurylphosphoric or dioctylphosphoric acids has been recommended to prevent corrosion in the presence of sea water [40].

Naphthenates, sorbitan esters or pentaerythritol esters and other substances are added to diesel and boiler fuels to inhibit rust.

Commercial rust inhibitors in concentrations of 0.008-0.01% by weight considerably reduce corrosion of fuel lines, pumps, gauges and tank cars [44]. Tank cars used in hauling fuel containing a rust inhibitor last for many years without protective coatings. In tests of a fuel with an additive in truck-trailer tanks over an 8-month period, 1/6 the amount of rust formed as compared with the results of tests run without the additive [44].

It was found on examination of gasoline-engine motor vehicles run on a gasoline containing rust inhibitor that no corrosion was in evidence in the carburetors, pumps, and gasoline tanks; the number of [replacement] carburetors and pumps used by these vehicles was reduced by 75% [44].

Rust inhibitors are usually added to the fuel when it is to be shipped by tanker.

Rust inhibitors are added to automotive gasolines in concentrations up to 3 mg/100 ml of the active component, to aviation gasolines in quantities up to 6 mg/100 ml (of the entire additive) [23] and to jet, diesel and distillate boiler fuels in approximately the same quantity [22].

Ammonium sulfonates and organic phosphorus compounds have come into most extensive use as commercial rust inhibitors.

Rust inhibitors are, for the most part, compounds that are soluble in the fuel, and they do not prevent corrosion in a water layer under the fuel. Water-soluble inhibitors such as sodium nitrite in combination with alkaline materials are used for this purpose. Such inhibitors can be added directly to the tank [22].

When fuels are used in engines operating near full load, where the temperature in the fuel system may rise high, corrosion of the metal by fuel oxidation products is intensified manifold. The corrosi

products may form a considerable fraction of the insoluble deposits and sludges that form at high temperatures in the fuel systems of jet and diesel engines; consequently, additives intended to improve the operational properties of such fuels must possess anticorrosion properties or contain special anticorrosion agents.

Reduction of Corrosion Due to Sulfur Compounds in Fuels

Active sulfur compounds in fuels (elementary sulfur, hydrogen sulfide, mercaptans) may cause corrosion of metals even at normal temperature. When this happens, mercaptides (of copper or cadmium) form on nonferrous-metal components (screens, filters, coatings, etc.), taking the form of deposits that are not soluble in the fuel.

TABLE 79

Inhibition of Corrosion on Steel (Inhibition Coefficient*) in High-Sulfur Automotive Gasoline in the Presence of Inhibitor over 54 Days [46]

| 1 Сталь | 2 Концентрация ингибитора в бензине | 3 Среда | | |
|---|---|---|---|---|
| | | 4 паровая фаза | 5 фаза топлива | 6 фаза воды и топлива |
| 7 СХЛ-1 | 0,01 | 22 | — | 13,5 |
| 10 СХЛ-4 | | 8 Полная защита | Полная защита | 3,7 |
| 11 4С | | 9 То же | То же | 2,6 |
| 12 Л-62 | | — | 61 | — |
| 7 СХЛ-1 | 0,02 | 8 Полная защита | 8 Полная защита | 6,0 |
| 10 СХЛ-4 | | 2,6 | 9 То же | 2,5 |
| 11 4С | | 2,4 | » | 6,1 |
| 12 Л-62 | | — | 7,6 | — |
| 7 СХЛ-1 | 0,05 | 8 Полная защита | 8 Полная защита | 8 Полная защита |
| 10 СХЛ-4 | | 9 То же | 9 То же | 9 То же |
| 11 4С | | » | » | » |
| 12 Л-62 | | — | 2,9 | — |

*The inhibition coefficient indicates the factor by which corrosion is reduced as compared with uninhibited gasoline.

1) Steel; 2) concentration of inhibitor in gasoline; 3) medium; 4) vapor phase; 5) fuel phase; 6) water-and-fuel phase; 7) SKhL-1; 8) complete protection; 9) same; 10) SKhL-4; 11) 4S; 12) L-62.

On combustion of the fuel, all sulfur compounds form aggressive oxides of sulfur, which may produce both gaseous corrosion and acid corrosion in an engine that has not been thoroughly warmed up or has been allowed to cool off, as a result of formation of the aggressive sulfuric acid on condensation of the water [45].

Additives for prevention of corrosion produced by active sulfur compounds in liquid fuel have not yet been adequately developed.

Corrosion of copper by sulfur in hydrocarbons was reduced considerably on addition of anthraquinone, aniline, triethanolamine, quinoline, benzyl alcohol, pyrogallol, α-naphthylamine, phthalic anhydride, phthalimide and other compounds [39]. The protective action of these inhibitors was expressed basically in an increased induction period before onset of corrosion. Anthraquinone added in quantities of 0.2% provided full corrosion protection for copper for about 2 years, while use of a fuel without additive resulted in formation of a sulfide layer on the copper in a few seconds [39]. Under the test conditions, the various substances prolonged the induction (from 50 min to 18 days); benzoyl peroxide and tetralin retarded the appearance of corrosion on copper by more than 100 days [39].

Bronze and brass components of diesel-engine fuel apparatus are protected from corrosion by sulfur-containing fuels (formation of mercaptides) by the use of additives containing metals deactivators [28, 30]. Commercial additives of the polar-polymer type were noted to give an anticorrosive effect for sulfur-containing diesel and boiler fuels [35].

An inhibitor prepared from ammonia and benzoic acid (AMBA) exhibits high effectiveness in protecting steels against corrosion by sulfur-containing fuels in the presence of water [46]. Table 79 illustrates the corrosion retardation produced by these materials for vari-

ous steels in sulfur-containing (0.1%) automotive gasoline.

Tests of the inhibitor under operational conditions (in stationary tanks and tankers), using sulfur-containing automotive gasoline, diesel fuel and crude petroleum, indicated that a 0.01% concentration of the inhibitor would provide the tanks with full corrosion protection. The inhibitor may be introduced into the fuel by spraying the surface of the empty tank or introduced into the ballast sea water [46].

Anticorrosion lubricating-oil additives are being used successfully to prevent corrosion and wear of engines by products of combustion of sulfur-containing (diesel) fuel, but the greatest gain is achieved when special anticorrosion agents are added to the fuel simultaneously. B.V. Losikov and S.E. Kreyn obtained encouraging results with such a combination when diesel fuels containing more than 1% of sulfur were used; aliphatic amines with molecular weights from 85 to 90 and containing 9-11% of nitrogen [1] were added to the fuel as an anticorrosion additive.

Zinc naphthenate has also been successfully tested as an anticorrosion additive to high-sulfur diesel fuels containing about 1% of sulfur; it is recommended that it be used in combination with an antiscaling additive to the lubricating oil [47]. The addition of 0.3% of zinc naphthenate made it possible to reduce wear by approximately half and thereby reduce it to the values characteristic for low-sulfur fuels.

Excellent results were also obtained on addition of alkali-metal nitrates and carbonates to high-sulfur diesel fuel. Wear of the piston rings was reduced considerably in all engines where the fuel with the additive was employed.

Additives that reduce corrosion by fuel-combustion products [48] exert their influence by neutralizing sulfur oxides and converting them to noncorrosive compounds that are carried out with the exhaust

gases. Under the conditions of combustion, these additives form compounds that react chemically with sulfur trioxide or sulfuric acid. For example, alkali-metal nitrates may produce nitrites or oxides of these metals, which then react with sulfur trioxide to form neutral or volatile products [48]. Alkali-metal carbonates can act by the same mechanism. Naphthenates of metals (zinc naphthenate) may, on combustion, form compounds that protect the surface of the metal from attack by the sulfur oxides [47].

Neutralizing additives may be introduced directly into the engine's fuel system [45]. When an ammonium salt is added in this way to a high-sulfur (1.25% S) diesel fuel, piston-ring scorching and varnish formation were eliminated completely and corrosive wear was reduced to a minimum.

The additive has a neutralizing effect and retards formation of the aggressive sulfur trioxide [45].

## ADDITIVES THAT IMPROVE OPERATIONAL PROPERTIES OF FUELS AT LOW TEMPERATURES

Difficulties arise in operation with fuels under low-temperature conditions, both as a result of changes in the properties of the fuel themselves, and as a result of freezing of water dissolved in the fuel or present in the air.

### Prevention of Changes in Fuel Properties at Low Temperatures

Low-temperature changes in a fuel that involve its chemical composition are manifested in separation of crystals of solidified hydrocarbons from it, increased viscosity, and freezing of the fuel. This applies principally to diesel and jet fuels produced from paraffinic petroleums [38, 49].

In addition to appropriate purification (deparaffinization), the use of certain special depressor additives can also improve the low-

TABLE 80

Influence of AzNII Depressor on Low-Temperature Properties of Diesel Fuels [49]

| 1 Топливо | 2 Концентрация присадки, % вес. | 3 Низкотемпературные свойства топлива | |
|---|---|---|---|
| | | 4 температура помутнения, °С | 5 температура застывания, °С |
| 6 Дизельное топливо летнее | 7 Без присадки | −6 | −12 |
| 8 То же | 0,3 | −7 | −26 |
| " | 0,5 | −8 | −28 |
| " | 1,0 | −10 | −32 |
| 9 Дизельное топливо зимнее | Без присадки | −49 | 10 −66 |
| 8 То же | 7 0,5 | −53 | Ниже −70 |
| 11 Газойль сураханский тяжелый | Без присадки | +5 | −16 |
| 8 То же | 7 1,0 | 0 | −25 |
| 12 Газойль сураханский | Без присадки | −4 | −7 |
| 8 То же | 1,0 | −7 | −25 |
| 13 Смесь 60% сураханского соляр. дистиллята и 40% сураханского керосина | 7 Без присадки | +1 | −4 |
| 8 То же | 1,0 | −1 | −31 |
| 14 Смесь 60% сураханского соляр. дистиллята и 40% доссорского керосина | 7 Без присадки | 0 | −5 |
| 8 То же | 1,0 | −3 | −50 |

1) Fuel; 2) additive concentration, % by weight; 3) low-temperature properties of fuels; 4) clouding temperature, °C; 5) pour point, °C; 6) summer-grade diesel fuel; 7) without additive; 8) same; 9) winter-grade diesel fuel; 10) below −70; 11) heavy Surakhany gas oil; 12) Surakhany gas oil; 13) mixture of 60% Surakhany solar distillate and 40% of Surakhany kerosene; 14) mixture of 60% of Surakhany solar distillate and 40% of Dossor kerosene.

temperature properties of fuels. They are added to diesel fuel to lower its pour-point temperature and improve pumpability at low temperatures. Depressors developed for lubricating oils and certain other substances are the basic materials used for this purpose.

The following depressors are used for lubricating oils and diesel fuels: condensation products of nonpolar organic compounds, e.g., of naphthalene with a chlorinated paraffin (Paraflow, AzNII depressor), etc.; condensation products of polar compounds (or of a nonpolar with a polar compound) — Santopure, paraffin-phenol, etc.; Voltolizing products — Voltols, soaps of multivalent cations, oxidation products of high-molecular hydrocarbons [38, 49, 1].

The action of the depressors is accounted for by adsorption of the additive by the fine paraffin crystals, so that growth of these crystals and formation of the crystal lattice are inhibited; it impedes adsorption of liquid hydrocarbons by the paraffin, preventing formation of gels [38, 22]. Other explanations have also been given for the action of the depressors. It is believed that they convert the steric structure of the paraffins into a compact structure [38], which would explain the coagulating action of the additive and the improved filterability of hydrocarbons with additives. The action of the depressors is also accounted for by the fact that, dissolving in the hydrocarbons, they act as crystallization centers about which paraffin crystals group; this retards the formation of a crystal lattice and improves the fluidity of the hydrocarbon product [38].

The influence of a depressor on the pour point of a diesel fuel is illustrated in Table 80.

It will be seen from these data that while it reduces the pour point considerably, the depressor has virtually no influence on the cloud point of the fuels, i.e., it does not inhibit the beginning of paraffin crystallization, but does retard the growth of the crystals [49].

The effectiveness of the depressor depends on the chemical composition of the fuel and the additive concentration (Table 80). The first portions of additive have a more striking effect. An increase in the additive concentration above a certain limit produces practically no result.

Depressors are added only to fuels that have poor low-temperature properties, since they are useless in fuels that do not contain paraffins. The depressor concentration in distillate fuels ranges from 0.01 to 0.1% [49, 22].

Although depressors do not inhibit initial crystallization of paraffins and do not influence the limiting temperature of possible filtration of the fuels, they facilitate transportation and pumping of the fuel by virtue of the considerable pour-point depression [49].

**Elimination of Operational Difficulties Connected with Freezing of Water**

The operational difficulties that arise as a result of freezing of water are expressed chiefly in icing of automotive-engine carburetors in cold damp weather and in the formation of ice crystals in aviation fuels.

Among the various methods that prevent or eliminate these effects, we again find the use of certain additives.

a) Fuel additives that prevent icing of automotive-engine carburetors (antiicing additives)

There are two known types of antiicing additives, each acting by a different mechanism. Additives of the first type dissolve in water to lower its freezing point. Additives of the second type, which are surface-active substances, form envelopes on ice particles, and this prevents their combining with one another or settling on the carburetor walls [23].

Various alcohols, glycols, formamides and derivatives thereof are used as antiicing additives of the first type. The additives are used in quantities up to 0.5-2% [23, 1]. For example, diethylene glycol monobutyl ether is added to gasoline in a concentration of 0.05-0.5% by weight [50].

Amines, ammonium phosphates, and other substances are used as additives of the second type [23].

A test of the effectiveness of an antiicing additive on 56 vehicles resulted in 10 cases of engine trouble (due to carburetor icing) in operation on a fuel with the additive, as against 511 in operation on

fuel without the additive [52].

Antiicing additives also prevent freezing of water in gasoline tanks and fuel pumps [51].

Also known as antiicing additives are such compounds as dimethylcarbinol with a solvent, branched glycols, such as 2-methylpentanediol-2,4 dimethylformamide, glycerine monooleate, etc. [23].

b) Additives that prevent formation of ice crystals in aviation fuels

Ice crystals form in both aviation gasolines and fuels for jet engines; this presents a great danger in the operation of aircraft.

The use of fuel additives is an excellent way to counter this effect.

Certain alcohols, ethers and special fluids that form low-freezing mixtures with water [49, 53, 57] may be used as such additives.

The additives are used in the fuel in quantities ranging from 0.1 to 0.5-1.0% by weight.

TABLE 81

Rate of Solution of Ice Crystals in Fuel with Addition of Additive [53, 49]

| 1 Количество кристаллов льда в топливе, % вес | 2 Температура топлива, °С | 3 Количество присадки, добавленной к топливу, % вес. | 4 Время растворения кристаллов, мин. |
|---|---|---|---|
| 0,01 | —40 | 0,1 | 60 |
| 0,01 | —40 | 0,3 | 31 |
| 0,01 | —30 | 0,1 | 35 |
| 0,01 | —30 | 0,3 | 17 |
| 0,05 | —20 | 0,1 | 51 |
| 0,05 | —20 | 0,3 | 28 |
| 0,05 | — 5 | 0,3 | 3 |
| 0,1 | —20 | 0,3 | 45 |
| 0,1 | — 5 | 0,3 | 5 |

1) Quantity of ice crystals in fuel, % by weight; 2) temperature of fuel, °C; 3) quantity of additive added to fuel, % by weight; 4) time for solution of crystals, minutes.

Successful application of isopropyl, methyl or ethyl alcohol,

tetra-, penta- or hexaethylene glycols [23, 1] and other such compounds for this purpose has been reported. Table 81 shows the influence of one of the additives on fuel filterability at low temperatures and its solvent action.

Additives not only prevent formation of ice crystals in the fuel; they also eliminate crystals that have already formed.

Antiicing agents and additives used to prevent formation of ice crystals have no detrimental effect on other properties of the fuel.

## ADDITIVES THAT PREVENT ACCUMULATION OF STATIC ELECTRICITY IN FUELS

Charges of static electricity may form in fuels when tanks are filled or when the fuel is transferred and filtered. Due to the low conductivities of hydrocarbons, these charges are not led away through the tank and apparatus walls and the strength of the resulting electric field may reach considerable values.

TABLE 82

Conductivities of Certain Petroleum Products [54]

| 1 Нефтепродукт | 2 Проводимость*, пикомы$^{-1}$ м$^{-1}$ |
|---|---|
| 3 Автомобильный бензин | 0,02—1 |
| 4 Керосин | 0,3—10 |
| 5 Дизельное топливо | 0,02—40 |
| 6 Нефть | 1500—70000 |

*A picoohm is $10^{-12}$ ohm.

1) Petroleum product; 2) conductivity,* picoohms$^{-1}$ m$^{-1}$; 3) automobile gasoline; 4) kerosene; 5) diesel fuel; 6) crude petroleum.

Very strong fields form when petroleum products are pumped at high speeds, particularly if they are contaminated by impurities or contain water [54]. Here, discharge of the static electricity in the form of sparks may take place, and produce fires and explosions. In

TABLE 83

Concentration of Certain Compounds Necessary to Produce Hydrocarbon Conductivities of 1000 picoohms$^{-1}$ m$^{-1}$ [54]

| 1 Сорт топлива | 2* Присадка | 3 Концентрация, кг/1000 м³ |
|---|---|---|
| 4 Бензол | 5 Тетраизоамиланикриновокислый аммоний . . . | 53 |
| 6 Лигроин | 7 Олеат марганца . . . . . | 293 |
| 8 Бензин | 9 Раствор Са-соли ди (2-этилгексил) сульфосукциниловой кислоты (Са-аэрозоль) . . . . . | 2000 |
| 10 Бензол | 11 Диизопропилсалицилат Са . . . . . | 2400 |
| 12 Бензин | 13 Раствор Cr-соли смеси моно- и диалкилсалициловых кислот (Cr-Ac) . . . . . | 6,2 |
| 14 Бензин | 15 «Антистатическая» присадка фирмы «Шелл» | 2 |

1) Fuel grade; 2) additive; 3) concentration, kg/1000 m$^3$; 4) benzene; 5) ammonium tetraisoamyl picrate; 6) ligroin; 7) manganese oleate; 8) gasoline; 9) solution of Ca salt of di(2-ethylhexyl)sulfosuccinic acid (Ca-aerosol); 10) benzene; 11) Ca diisopropylsalicylate; 12) gasoline; 13) solution of Cr salt of mixture of mono- and dialkylsalicylic acids (Cr-Ac); 14) gasoline; 15) Shell "antistatic" additive.

the majority of cases, the discharges take place at projecting parts of the tank (corrosion caverns, etc.), and sometimes directly in the body of the liquid [55]. In the majority of cases, inside-tank explosions have been observed while they were being filled, particularly with severe agitation and when water has been allowed to settle out.

Clear petroleum products, i.e., all distillate fuels, are particularly dangerous as regards accumulation of static electricity, since they possess the lowest conductivities (Table 82).

Additives that raise the conductivities of fuels [54, 55] are employed to eliminate the danger of explosions due to accumulation of static electricity.

The conductivity must be raised to values that guarantee rapid diversion of charges to the walls of the apparatus and tanks.

When the conductivity is raised to 20-50 picoohms$^{-1}$ m$^{-1}$, the electric field is sharply weakened. When fuels are pumped at a speed of

~10 m/sec or when they are filtered, the conductivity should be ~500 picoohms$^{-1}$ m$^{-1}$ to guarantee dissipation of the charges. Petroleum products with conductivities above 1000 picoohms$^{-1}$ m$^{-1}$ are safe as regards static-electricity accumulation in any operation [54].

Certain (calcium, chromium) salts of organic acids, oleates and other compounds have been investigated for use as additives to raise the conductivities of fuels ("antistatic" additives). Table 83 lists the concentrations of certain additives necessary to guarantee safe conductivity values in the fuels.

The Ca-aerosol additive contains 2% by weight of calcium and 55% of a neutral solvent, and has an average molecular weight of about 2000.

The Cr-Ac additive contains chromium salts of mono- and dialkylsalicylic acids whose alkyl chains consist of 14-18 carbon atoms; the additive contains 2.1% by weight of chromium and 30% of neutral solvent, and its average molecular weight is about 2500.

The phenomenon of synergism is observed when the additives are mixed: the combination of additives is found to be more effective than its components taken alone. The Shell additive has been found most effective. It is a mixture of equal quantities of the Ca-aerosol additive OT and the Cr-Ac additive and contains 42% of neutral solvent, 1.0% by weight of calcium and 1.05% by weight of chromium.

It is recommended that this additive be used in the fuel in quantities of 2 kg per 1000 m$^3$ of fuel. This concentration ensures safe operation with the fuel regardless of conditions. The additive is stable during storage. To introduce the additive into the fuel, a solution containing 0.4 kg/m$^3$ of fuel is prepared and then mixed with the fuel in the proper calculated quantity. The basic difficulty encountered in the use of the additive is that of storing it in the fuel in the presence of water. It was established in a check of the storability

TABLE 84

Relative Increase in Use of Fuel Additives in the USA [22, 23]

| 1 Присадки | 2 Топливо | 3 Потребление присадки, тыс. *т* в год | | | | |
|---|---|---|---|---|---|---|
| | | 1958 | 1959 | 1960 | 1961 | 1965 |
| 3а Этиловая жидкость (антидетонатор) | 4 Автомобильные бензины | 336,5 | 347 | 358 | — | 394 |
| | 5 Авиационные бензины | 42,3 | — | 31,4 | — | 23,5 |
| 6 Антинагарные * присадки | 4 Автомобильные бензины | 0,93 | 0,98 | 1,11 | — | 1,23 |
| 7 Антиокислители | 4 Автомобильные бензины | 3,04 | 3,11 | 3,21 | — | 3,54 |
| | 5 Авиационные бензины | 0,31 | — | 0,23 | — | 0,173 |
| 8 Ингибиторы коррозии | 4 Автомобильные бензины | 1,81 | 1,85 | 1,95 | — | 2,13 |
| | 5 Авиационные бензины | 0,258 | 0,19 | 0,19 | — | 0,145 |
| | 9 Реактивные топлива | 0,272 | 0,303 | 0,331 | 0,349 | — |
| | 10 Дизельные топлива | 1,065 | 1,089 | 1,11 | 1,138 | — |
| | 11 Дистиллятные котельные топлива | 1,695 | 1,765 | 1,84 | 1,91 | — |
| 12 Деактиваторы металла (активный компонент) | 4 Автомобильные бензины | 0,589 | 0,634 | 0,634 | — | 0,725 |
| | 10 Дизельные топлива | 0,039 | 0,04 | 0,0408 | 0,0416 | — |
| | 11 Дистиллятные котельные топлива | 0,0625 | 0,0652 | 0,0679 | 0,07 | — |
| 13 Стабилизаторы-диспергенты | 10 Дизельные топлива | 1,21 | 1,238 | 1,263 | 1,291 | — |
| | 11 Дистиллятные котельные топлива | 1,925 | 2,0 | 2,085 | 2,16 | — |
| 14 Депрессаторы | 10 Дизельные топлива | 0,0181 | 0,0208 | 0,0213 | 0,0217 | — |
| | 11 Дистиллятные котельные топлива | 0,0322 | 0,034 | 0,0349 | 0,0363 | — |
| 15 Красители | 4 Автомобильные бензины | 0,363 | 0,372 | 0,385 | — | 0,426 |
| | 5 Авиационные бензины | 0,0294 | — | 0,0213 | — | 0,0163 |

*According to another source, the quantity of antiscaling additives used in 1959 was 3.6 thousand tons/year [1].

1) Additive; 2) fuel; 3) amount of additive, thousands of tons per year; 3a) ethyl fluid (antiknock compound); 4) automobile gasolines; 5) aviation gasolines; 6) antiscaling additive*; 7) antioxidants; 8) corrosion inhibitors; 9) jet fuels; 10) diesel fuels; 11) distillate boiler fuels; 12) metals deactivators (active component); 13) stabilizer detergents; 14) depressors; 15) dyes.

of the additive in ligroin that was being shipped by tanker that the conductivity of the ligroin had dropped by the time it had been unloaded from the tanker as compared with its initial value (950 and 2200 picoohms$^{-1}$ m$^{-1}$, respectively), but that the conductivity still remained sufficiently high [54].

It should be noted that additives that raise the conductivities of fuels ensure protection from discharges only in cases where low conductivity of the fuel is the chief cause of charge accumulation and, consequently, addition of the additive to the fuel does not eliminate the necessity for grounding the tank.

* *
*

Fuel additives deliver considerable qualitative and economic gains, and this has been responsible for the intensive development of their application. For the sake of illustration, Table 84 presents figures that characterize the relative increase in the amounts of additives used in the USA during recent years and the prospects for continued increase in the next few years [22, 23].

In 1960, a total of 404 thousand tons of additives were used; of this, about 397 thousand tons were used in gasolines and about 7 thousand tons in other distillate fuels.

Antiknock substances compose the basic quantity of additives used in gasolines: about 358 thousand tons per year, while the remaining gasoline additives make up about 39 thousand tons per year.

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[Footnotes]

404 A commercial additive produced in the USA to improve combustion of diesel fuels.

406 The so-called scale "modifiers."

## Chapter 15

## ANTIKNOCK COMPOUNDS

Antiknock compounds are additives that raise the detonation stability of fuels.

Metal-organic compounds and organic materials (e.g., hydrogen compounds, ethers, and so forth) have been investigated as antiknock additives. The metal-organic compounds are considerably more effective (Table 85); they are added to gasolines in concentrations ranging up to several tenths of a percent.

Lead compounds and compounds of tin, thallium, bismuth, selenium, tellurium, manganese, iron, cobalt, nickel, copper, chromium, indium and a number of other metals possess antiknock properties [1]. Alkyl metals, carbonyls, internal-complex metal salts and certain other types of compounds have been extensively investigated as antiknock additives [1]. In recent years, metal-organic compounds of a new type – the cyclopentadienyl compounds – have come under extensive scrutiny [22 – 24, 34, 35].

Organic antiknock compounds are less effective and are therefore added to the gasolines in considerably larger concentrations (ranging in practice up to 4%) [18]. Normally, organic compounds are employed only in combination with tetraethyl lead to lower consumption of high-octane gasoline components.

In addition to high effectiveness, an antiknock compound must have a number of other necessary properties: satisfactory solubility in gasolines; stability in storage, including stability in gasoline

solutions; the possibility of sufficiently complete "scavenging" of the combustion products from the engine's cylinders, even though special scavengers may be required; adequate volatility to prevent formation of deposits in the engine's induction system, and so forth. Nontoxicity is yet another important property of the antiknock compound.

This complex of specifications is, with the exception of toxicity, most completely satisfied by tetraethyl lead, which is, at the present time, the only antiknock substance that has come into practical use.

Antiknock agents are necessary for both aviation and automotive gasolines, although the future of antiknock compounds is associated principally with the development of reciprocating automotive engines [15, 16, 25, 36 – 41, 43], since the basic engines now in use in aviation are jet types.

TABLE 85

Relative Effectiveness of Antiknock Agents [1, 2]*

| 1 Антидетонаторы | 2 Формула | 3 Относительная эффективность по критической степени сжатия |
|---|---|---|
| 4 *Органические* | | |
| 5 Анилин | $C_6H_5NH_2$ | 13,5 |
| 6 Ксилидин | $C_6H_3(CH_3)_2NH_2$ | 15,0 |
| 7 *Металлоорганические* | | |
| 8 Тетраэтилолово | $Sn(C_2H_5)_4$ | 25,0 |
| 9 Диэтилселен | $Se(C_2H_5)_2$ | 60,0 |
| 10 Диэтилтеллур | $Te(C_2H_5)_2$ | 200,0 |
| 11 Тетракарбонилникель | $Ni(CO)_4$ | 300,0 |
| 12 Пентакарбонилжелезо | $Fe(CO)_5$ | 300,0 |
| 13 Тетраэтилсвинец | $Pb(C_2H_5)_4$ | 600,0 |

*The effectiveness of benzene is taken as unity.

1) Antiknock compounds; 2) formula; 3) relative effectiveness based on critical compression ratio; 4) organic; 5) aniline; 6) xylidine; 7) metal-organic; 8) tetraethyl; 9) diethyl selenium; 10) diethyl tellurium; 11) tetracarbonyl nickel; 12) tetracarbonyl iron; 13) tetraethyl lead.

TETRAETHYL LEAD

Tetraethyl lead was first prepared in 1852, but not until 1921 was a practical application found for it, and it remained an uncommon laboratory preparation [1].

In 1921, Kettering, Midgely and Boyd [6] discovered the antiknock properties of tetraethyl lead.

From the very beginning, the TES [tetraethyl lead]-based antiknock agent was produced in the form of ethyl fluid, which is a mixture of TES and lead "scavengers" – halogenoalkyls.

At the present time, the production of TES in the USA runs to about 210 thousand tons/year [43] and still shows a tendency toward further increases (Fig. 126), as is the case in other countries as well.

The industrial method of producing tetraethyl lead is based on the reaction of a lead-sodium alloy with ethyl chloride:

$$4PbNa + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl.$$

Rock salt, lead, and cracking gas or ethyl alcohol are the initial materials for the production of TES [1].

Metallic sodium and chlorine are produced by electrolysis of the rock salt. The former is fused with lead to produce a lead-sodium alloy containing 90% lead and 10% sodium.

Chlorine is used to produce hydrogen chloride. Ethyl chloride is obtained from hydrogen chloride and ethylene (or ethyl alcohol) in the presence of a catalyst. The TES is produced by the reaction indicated from the alloy and ethyl chloride. The temperature in the reactors is held at 40 – 60°, and the reaction takes 2 – 6 hours. The ethyl chloride is taken in a quantity of 120%, figured on the metallic sodium. Dimethylamine, triethylamine, pyridine, certain ethers and even metals such as zinc serve as the catalysts.

Tetraethyl lead is distilled with water from a mixture of products. The yield of tetraethyl lead is approximately 80% on the metallic sodium used.

At plants set in operation before 1957, TES is produced in batch-type reactors. In recent years, a more sophisticated production process has been developed for TES.

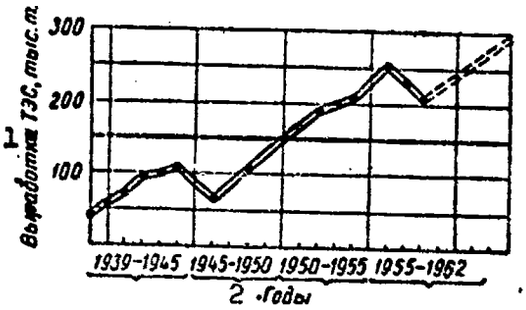



Fig. 126. Increase in TES [tetraethyl lead] production in the USA. 1) TES production, thousands of tons; 2) years.

At one of the plants in the USA – which was placed in operation in 1957 – TES is already in production by a continuous process.

Tetraethyl lead is a transparent colorless liquid with a specific gravity $d_4^{20} = 1.6524$, boiling at 200° with decomposition. It is not soluble in water, but has good solubility in hydrocarbons, as well as in alcohol, ether and acetone.

Thermal decomposition of TES forms metallic lead and the free ethyl metal:

$$Pb(C_2H_5)_4 \rightarrow Pb + 4C_2H_5.$$

At a temperature of 500 – 600°, TES decomposes completely in accordance with the above reaction. TES should be added to gasolines in concentrations no higher than 0.3 – 0.4% by weight (i.e., 3 – 4 g/kg), since further increases in its concentration have virtually no effect (Fig. 127). Gasolines of different chemical compositions are characterized by different "receptivities" to TES (Table 86).

Paraffinic hydrocarbons are most susceptible to TES; here, paraffinic hydrocarbons having lower octane numbers are more responsive to TES. Aromatic and unsaturated hydrocarbons are characterized by the lowest response to TES, while the naphthenic hydrocarbons occupy an intermediate position.

TABLE 86

Influence of TES on Antiknock Properties of Gasolines [13]

| 1 Топливо | 2 Преобладают углеводороды | 3 Октановое число (моторный метод) при содержании ТЭС, г/кг | | | | | 4 Прирост о. ч. от 3,3 г/кг ТЭС |
|---|---|---|---|---|---|---|---|
| | | 0 | 0,8 | 1,6 | 2,5 | 3,3 | |
| 5 Алкилбензол | 6 Ароматические | 96 | 98 | 99,5 | 100,5 | 101 | 5 |
| 7 Алкилат | 8 Изопарафины | 91 | 97 | 101 | 103 | 105 | 14 |
| 9 Бензин Б-70 из бакинских нефтей | 10 Нафтены | 70 | 80 | 85 | 87 | 89 | 19 |
| 11 Бензин грозненской парафинистой нефти | 12 Парафины | 59 | 70 | 79 | 84 | 86 | 27 |
| 13 Бензин каталитического крекинга | 14 Содержит 35% ароматических, 52% парафиновых углеводородов | 78 | 84 | 88 | 91 | 94 | 16 |
| 15 Бензин термического крекинга | 16 Содержит 45—50% непредельных, 39—44% парафиновых углеводородов | 70 | 79 | 81,5 | — | — | — |

1) Fuel; 2) hydrocarbons predominating; 3) octane number (motor method) at TES content in g/kg; 4) octane-number increase on addition of 3.3 g/kg of TES; 5) alkylbenzene; 6) aromatic; 7) alkylate; 8) isoparaffins; 9) B-70 gasoline from Baku petroleums; 10) naphthenes; 11) gasoline from Groznyy paraffinic petroleum; 12) paraffins; 13) catalytic-cracking gasoline; 14) contains 35% aromatic, 52% paraffinic hydrocarbons; 15) thermal-cracking gasoline; 16) contains 45-50% of unsaturated and 39-44% of paraffinic hydrocarbons.

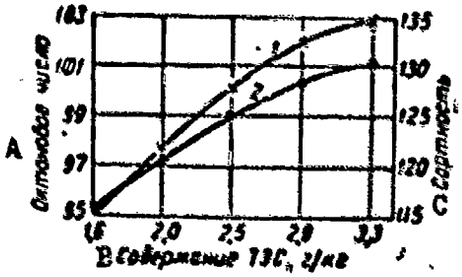



Fig. 127. Increase in octane number and performance number (on rich mixture) due to addition of TES to a mixture of 68% aviation base and 32% alkylate. 1) Performance number; 2) octane number. A) Octane number; B) TES content, g/kg; C) performance number.

TES is more effective in raising performance number than octane number in gasolines (see Fig. 127).

When sulfur compounds are present in gasolines, their receptivity to TES diminishes (Fig. 128); during storage, deposits precipitate from ethylated gasolines and the TES concentration diminishes. The strongest "antagonists" of TES among the sulfur

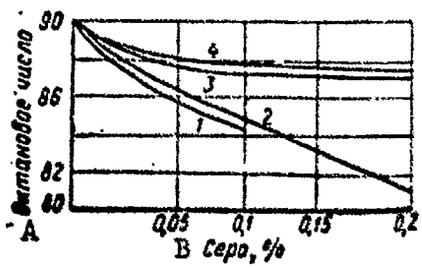



Fig. 128. Decrease in receptivity of gasolines to ethyl fluid in the presence of sulfur compounds [3]. 1) Butyl mercaptan; 2) dibutyl mercaptan; 3) dibutyl sulfide; 4) thiophene. A) octane number; B) sulfur, %.

compounds are the mercaptans and disulfides; these are followed by the thiophanes, sulfides and thiophenes. The aromatic sulfides and disulfides are less active in this respect than the corresponding alkyl sulfides and disulfides.

The detrimental influence of sulfur compounds on the antiknock properties of ethylated gasolines is apparently to be accounted for by the fact that the sulfur compounds enter into reaction with the TES during preparation of the mixture in the engine, and even earlier – during storage of the gasolines –, for example, according to the reaction

$$Pb(C_2H_5)_4 + 4RSH \rightarrow Pb(SR)_4 + 4C_2H_6$$

and lower the TES concentration [3].

MECHANISM OF ANTIKNOCK ACTION

Simultaneously with development of the theory of detonation (see Chapter 7), a theory was also developed to account for the mechanism by which artiknock agents act [1, 4].

The conditions under which tetraethyl lead decomposes were clarified as a result of research by various authors.

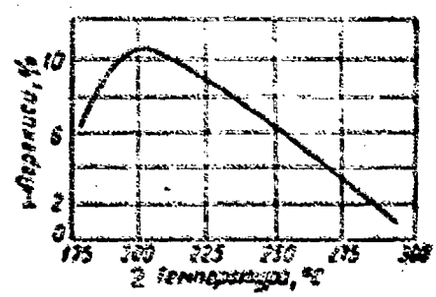



Fig. 129. Oxidation of n-heptane in the presence of ethyl fluid [3]. 1) peroxides, %; 2) temperature, °C.

The decomposition of TES begins at 200° [1]. The reaction of thermal decomposition of TES in the gaseous phase is monomolecular.

The thermal decomposition of TES (like that of other metal-organic compounds

of lead, tin and mercury) is autocatalytic and is accelerated on introduction of finely dispersed lead.

In the presence of TES, the concentration of the peroxides formed does not decline in hydrocarbon vapors when they are oxidized at temperatures below 200° (Fig. 129); as the temperature and decomposition rate of TES increase, the concentration of the peroxides drops off sharply [2, 3].

On the basis of the detonation theory (see Chapter 7) that he developed, A.S. Sokolik [2] proposed the following explanation for the mechanism by which metal-organic antiknock agents of the tetraethyllead type exert their influence. The first stresses the important role that must be taken by free radicals formed during decay of the metal-organic antidetonator. The introduction of free radicals should accelerate the chain process of peroxide decomposition in the cold-flame stage and reduce the concentration of these peroxides. It has been shown experimentally that the introduction of TES into an air-and-hydrocarbon mixture sharply weakens the primary cold flame, prolongs the secondary-flame delay and, finally, inhibits development of the hot explosion, shifting its range toward higher pressures.

The ability of the radicals formed on decomposition of TES to accelerate decomposition of the peroxides was demonstrated experimentally in experiments conducted in the liquid phase [4]. In this case, formation of metallic lead is apparently excluded, and acceleration of the peroxide-decay process takes place solely as a result of the action of the free radicals liberated in the decomposition of TES.

According to A.S. Sokolik, the role acquired by the metal in complete decomposition of TES comes into evidence in the later stages of the self-ignition process of the fuel-air mixture and amounts to deactivation of the active particles formed in explosive decomposition

of the peroxides.

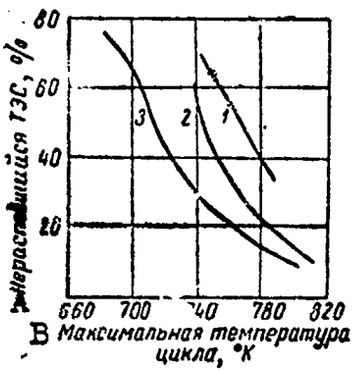



Fig. 130. Influence of chemical composition of fuel on decomposition of tetraethyl lead. 1) Diisobutylene; 2) isooctane; 3) 90% isooctane + 10% n-heptane. A) Undecomposed TES, %; B) maximum temperature of cycle, °K.

Certain features of the action of antiknock agents can be explained on the basis of the above premises.

**As the TES concentration in the fuel** rises, the rise in the antiknock effect becomes slower (see Fig. 127), and when a certain concentration limit is exceeded, further addition of TES may even encourage knocking. These effects are apparently to be accounted for by an increase in the free-radical concentration with increasing concentration of TES in the fuel; these radicals are formed on decomposition of TES in the pre-flame stages of the process. The free radicals can accelerate not only the decomposition of peroxides, but their formation as a result of initiation of hydrocarbon oxidation. With increasing concentration of TES above a certain limit, the latter process comes to predominate over the former.

At very high TES concentrations, there is a probability that single-stage volume ignition takes place as a result of a sharp drop in activation energy due to injection of large quantities of active initial centers into the gas [2].

Different hydrocarbon groups have differing receptivities to TES. The insignificant improvement of the antiknock properties of olefins and the absence of any positive effect on addition of TES to diolefins can be accounted for by the instability of the hydroxides of these hydrocarbons and their easy decomposition to form inactive products even without assistance from TES.

It has been shown experimentally [3] that during the pre-flame process in the engine, TES introduced into a solution of an olefin – diisobutylene – is "consumed" at a rate lower than when it is introduced into the engine in an isooctane solution (Fig. 130).

Benzene does not form peroxides, so that its octane number is not raised by addition of TES [7].

The mechanism by which other antiknock agents act has not yet been adequately illuminated at the present time.

LEAD "SCAVENGERS" AND ETHYL FLUID

During combustion of gasoline containing TES, lead oxide, which has a low "volatility," forms in the engine; since the melting point of lead oxide is rather high (888°), some of it (about 10% figured on the lead introduced with the gasoline [28]) is deposited in the form of a solid precipitate onto the combustion-chamber walls, spark plugs and valves; this quickly puts the engine out of commission.

Consequently, the widespread practical use of TES as an antiknock agent became possible only after Midgely applied special additives to the TES – the alkylhalides ($C_2H_5Br$ and $C_2H_4Br_2$) – which came to be known as lead "scavengers." The function of the "scavengers" consists in converting the products of oxidative decomposition of TES (metallic lead and lead oxide) into "volatile" halogen compounds of lead that have considerably higher vapor pressures:

$$2C_2H_5Br \rightarrow 2C_2H_4 + 2HBr,$$
$$PbO + 2HBr \rightarrow PbBr_2 + H_2O,$$
$$Pb + 2HBr \rightarrow PbBr_2 + H_2.$$

The melting points of halogen compounds of lead are rather low (e.g., 370° for $PbBr_2$); under the temperature conditions of an engine, these compounds are in the vapor state. It is believed [28] that the most complete scavenging of lead from the engine should be ensured by the thermally least stable compounds, which are capable of decompos-

quite completely even during the compression stroke, with liberation of the hydrogen halide (see above) or the free halogen.*

For the alkylhalides, an increase in the number of halogen atoms in the molecule lowers their thermal stability and, as has been shown by direct experiment on an engine, increases their effectiveness as lead scavengers (Fig. 131) [28].

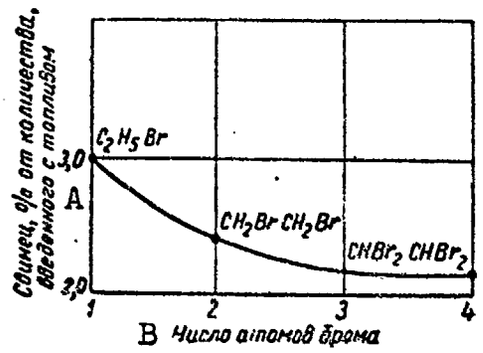



Fig. 131. Influence exerted by degree of substitution of hydrogen by bromine in halogen carrier upon deposition of lead in engine combustion chamber [28]. B-78 gasoline + 5 ml of TES (2.5 centimoles or 8.246 g) per 1 kg of fuel. A) Lead, % of quantity introduced with fuel; B) number of bromine atoms.

However, Macauley writes [29] that it is unfortunately not possible to choose the TES scavengers from among the compounds that are most effective as scavengers, basically for two reasons.

Firstly, thermally unstable halogen compounds are "antagonists" to TES and depress the octane number of ethylated gasoline by a considerable margin. For example, the tertiary compounds are the thermally least stable among the alkylchlorides; on addition of tertiary butyl- and amylchlorides to ethylated gasoline in proportions close to stoichiometric, the octane number of the gasoline is reduced by 2-6 points.

The mechanism of this effect is not yet sufficiently clear. It is assumed [3] that the thermally stable halogen compounds form the hydrogen halide (or halogen) at too low temperatures, and that these enter into reaction with the TES, reducing its concentration in the fuel-air mixture. This assumption is confirmed by the fact that, for example, HCl is a stronger "antagonist" to TES than are the alkylchlorides [30].

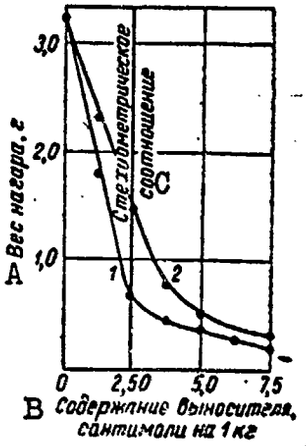



Fig. 132. Influence exerted by scavenger concentration on quantity of scale formed in combustion chamber with engine operating on ethylated gasoline [17] (conditions same as for Fig. 6). 1) Dibromoethane; 2) dichloroethane. A) Weight of scale, g; B) content of scavenger, centimoles per 1 kg; C) stoichiometric proportions.

Secondly, the halogen-organic compounds that are most effective as scavengers may react with TES even at the temperatures of storage; here, deposits form in ethyl fluid and in ethylated gasolines. Even Midgely observed these phenomena on addition of carbon tetrachloride to TES. After 1945, the firm "Ethyl Corporation" tested 45 new lead scavengers, but none of them was found satisfactory, basically because of their tendency toward undesirable reactions with TES under the conditions of storage [29]. Such compounds as 1,1,2-tribromoethane and 1,1,2,2-tetrabromoethane have also gone unused for the same reason [31].

At the present time, only alkylhalides with 1-2 halogen atoms and 2-3 carbon atoms in the molecule (ethyl bromide, dibromoethane, dichloroethane, and 1,2-bromopropane, see Table 87) are used in practice as lead scavengers.

The introduction of the scavengers together with the TES into gasolines in the stoichiometric proportions (2 atoms of halogen per 1 lead atom) raises the degree to which the lead is scavenged from the combustion chamber to 97-98% [28] (as against 90% without the scavenger), and has no influence on the gasoline's octane number; the latter does not change even when the scavenger concentration is doubled [30].

When the scavenger concentration is raised above the stoichiometric level, the degree to which lead is scavenged from the combustion chamber is increased by an additional small amount (Fig. 132).

However, substantial increases in the scavenger concentration in the gasoline are not permissible because of the increased combustion-chamber corrosion by the residual free hydrogen halide formed on decomposition of the scavenger. Thus, it was established in tests on aviation engines [32] that an increase of the scavenger content in the ethyl fluid by a factor of 1.5-2 over the stoichiometric proportions results in considerable acceleration of spark-plug and valve attrition. After 18 hours of operation of an aviation engine on ethylated gasoline with a doubled content of scavenger, the rate of valve corrosion was 5-6 times that observed in an engine operating on a gasoline with the normal scavenger content [32], although the quantity of the deposits in the first engine was much smaller. Normally, the scavenger excess is about 10-15% over the stoichiometric composition for those types of ethyl fluids in which only bromine compounds are used as scavengers (aviation ethyl fluid). If the ethyl fluid contains alkylchlorides and alkylbromides as scavengers, the scavenger content is made larger relative to the amount of TES. Thus, 1 mole of dichloroethane and 0.5 mole of dibromoethane are required per 1 mole of TES in American automotive ethyl fluid [30].

This is accounted for by the fact that the alkylchlorides are considerably less effective as lead scavengers than the alkylbromides; this can be seen even from Fig. 132. A particularly distinct difference between the effectivenesses of chlorine and bromine scavengers came to light in tests of a GAZ-MM automotive engine on gasolines containing 3 ml/kg of ethyl fluid with two different scavengers – ethyl bromide and dichloroethane [3]. The engine operated normally for 247 hours on the ethylated gasoline with ethyl bromide (the entire test period). In the engine tested on the gasoline containing dichloroethane as a scavenger, the plugs failed after only 10 hours of opera-

tion as a result of lead deposition, and the valves burned out after 76 hours.

TABLE 87

Physical Properties of Lead Scavengers [1]

| 1 Показатели | 2 Бромистый этил | 3 Дибром-этан | 4 Хлористый этил | 5 Дибром-пропан |
|---|---|---|---|---|
| 6 Удельный вес при 20° С . . . | 1,460 | 2,182 | 0,8943 | 1,933 |
| 7 Вязкость при 15° С, *сст* . . . | 4,18 | 1,88 | 0,28 | — |
| 8 Температура кипения, °С . . | 34,4 | 131,7 | 12.5 | 141,6 |
| 9 Температура плавления, °С . | —119 | +10 | —138,7 | —55,5 |
| 10 Упругость паров по Рейду при 20° С, *мм* рт. ст. . . . | 399 | 8,75 | 1044.24 | 5,82 |

1) Indicator; 2) ethyl bromide; 3) dibromoethane; 4) ethyl chloride; 5) dibromopropane; 6) specific gravity at 20°C; 7) viscosity at 15°C, cst; 8) boiling point, °C; 9) melting point, °C; 10) Reid vapor pressure at 20°C, mm Hg.

The lower effectiveness of alkylchlorides as lead scavengers as compared with the alkylbromides is accounted for by the lower "volatility" (i.e., lower vapor pressure) of the chlorine compounds of lead as compared with its bromine compounds [33].

Aside from their effectiveness, the scavengers differ in a number of physical properties that are important from an operational standpoint (Table 87).

Dibromopropane, which has a boiling point near that of TES, is a superior scavenger; the curves of vapor pressure as a function of temperature for dibromopropane and TES are also similar, and this ensures the most uniform metering of TES and scavenger among the cylinders of the engine [3]. Unlike ethyl bromide, dibromopropane does not evaporate from the gasolines during storage and, unlike dibromoethane, it does not crystallize out of the ethyl fluid when the temperature drops below -5 to -8°.

TYPES OF ETHYL FLUID

The different types of ethyl fluid contain different scavengers (Table 88). The basic types of ethyl fluid have not undergone any essential changes in the postwar years, either as regards their composition or as regards their standardized physicochemical indices.

**The new type P-2 ethyl fluid, which contains dibromopropane as a** scavenger and is superior to other types of ethyl fluid by virtue of its operational properties, has been developed in the USSR.

Only bromine-based scavengers are employed in the USSR. A mixture of alkylbromides and chlorides is used in the automotive fluids produced in the USA and other countries. 1 ml of R-9 fluid is equivalent in antiknock effect to 0.8 ml of 1-TS fluid or 0.9 ml of P-2 fluid.

Two new problems that are of great practical importance for operations arose during the postwar years in application of ethyl fluid and ethylated gasolines. It was found that during storage, the ethyl fluid may undergo "aging." The content of trialkyl lead compounds in it increases sharply, and, after a certain time, a deposit consisting of various insoluble lead compounds makes its appearance.

Ethylated gasolines are stabilized with antioxidants to prevent decomposition of TES during their storage. The receptiveness of gasolines containing "aged" ethyl fluid to antioxidants diminishes sharply and the stability level of the ethylated gasolines to which this ethyl fluid is added drops accordingly.

Accordingly, the [Soviet] technical specifications provide for introduction of the ethyl fluid at the point at which the antioxidant (p-hydroxydiphenylamine) is produced in a concentration of 0.02-0.03% by weight; this prevents aging of the ethyl fluid during storage. Simultaneously, provision is made for determining the stability period of the solution of stabilized ethyl fluid in n-heptane at the point of production. The stability period, i.e., the time from the beginning of

TABLE 88

Composition of Various Types of Ethyl Fluid

| 1 Компоненты | 2 Жидкости СССР | | | 6 Жидкости США, Англии, ФРГ [18, 1, 26, 27] | | | |
|---|---|---|---|---|---|---|---|
| | 3 Р-9 | 4 1-ТС | 5 П-2 | 7 1-Т авиационная | 8 О-62 автомобильная | Q | 9 Тип I |
| 10 ТЭС в % вес не менее . . . | 54,0 | 58,0 | 55,0 | 61,41 | 61,48 | 63,3 | 54,5 |
| Бромистый этил в % вес. не менее 11 . . . . . | 33,0 | — | — | — | — | — | — |
| Дибромэтан в % вес. не менее 12 . . . . . | — | 36,0 | — | 35,68 | 17,86 | 25,75 | 36,4 |
| Дихлорэтан в % вес. не менее 13 . . . . . | — | — | — | — | 18,81 | 8,72 | — |
| Дибромпропан в % вес. не менее 14 . . . . . 15. | — | — | 34,4 | — | — | — | — |
| α-Монохлорнафталин, % вес. | 6,8 ± 0,5 | — | 5,5 | — | — | — | 9,0 |
| Красители, % вес. 16 . . . | 0,1 | 0,5 | 0,1 | 0,05 | 0,12 | 2,23 | 0,1 |
| Наполнитель (керосин или 17 бензин) . . . . . | Остальное количество 18 – (до 100%) | | | | | | — |

1) Components; 2) fluids used in USSR; 3) R-9; 4) 1-TS; 5) P-2; 6) fluids used in USA, England, and West Germany [18, 1, 26, 27]; 7) 1-T aviation; 8) O-62 automotive; 9) type I; 10) TES in % by weight no less than; 11) ethyl bromide in % by weight no less than; 12) dibromoethane in % by weight no less than; 13) dichloroethane in % by weight no less than; 14) dibromopropane in % by weight no less than; 15) α-monochloronaphthalene, % by weight; 16) dyes, % by weight; 17) vehicle (kerosene or gasoline); 18) remainder (to 100%).

oxidation of the heptane solution of ethyl fluid at 100° to the onset of decomposition of the TES, as determined from the turbidity, should be no less than 7 hours.

Problems related to the decomposition of TES in aviation gasoline during storage are considered in detail in Chapter 18.

In automotive engines having high compression ratios (α = 9 to 12), the problem of scaling acquires great practical importance. With the engine operating on ethylated gasoline, scales consisting of 60-90% lead form in the combustion chamber and cause serious difficulties in operation. Glowing scale particles are sources of spontaneous, uncontrolled "surface" ignition of the mixture. These scales contribute to premature failure of spark plugs and raise the octane-number re-

quirement of the engine.

The addition of special phosphorus-containing additives to ethylated automotive gasolines is a rather effective way of countering the detrimental influence of scale on engine operation.

Phosphorus is the most effective of the known "antagonists" of TES; consequently, the phosphorus additives should be introduced in minimal concentrations in order not to depress the antiknock properties of the gasolines [30].

PENTACARBONYL IRON (PKZh) AND DICYCLOPENTADIENYL IRON (FERROCENE)

Pentacarbonyl iron $Fe(CO)_5$ is one of the first metal-organic antiknock agents subjected to extensive testing in engines after TES [17]. The antiknock properties of pentacarbonyl iron (PKZh) were discovered at the beginning of the nineteen-twenties.

Pentacarbonyl iron is produced as a result of the reaction of carbon monoxide with reduced metallic iron at high pressures and temperatures.

Pentacarbonyl iron is a pale yellow liquid with a specific gravity $d_4^{20} = 1.457$, a boiling point of $102.5^\circ$, and a melting point of $-21^\circ$; it is not soluble in water. It decomposes in light with formation of a solid precipitate $Fe(CO)_9$, which is capable of self-ignition; it is nontoxic. Pentacarbonyl iron is about 15-20% inferior to TES as regards effectiveness (see Table 85); it is usually added to the fuel in a concentration of 0.2-0.8% by volume.

Tests of automotive, aviation and tractor [17] engines operating on fuels with PKZh showed that deposits of ferric oxide form in the engine's combustion chambers and result in premature wear and burnout of the valves. Halogen compounds are not effective as scavengers with respect to PKZh. On combustion of a fuel containing PKZh and halogen compounds, it is basically $Fe_2O_3$ that forms rather than the halogen

compounds of iron [2]. Due to the lack of effective scavengers, PKZh has not come into practical use as an antiknock agent.

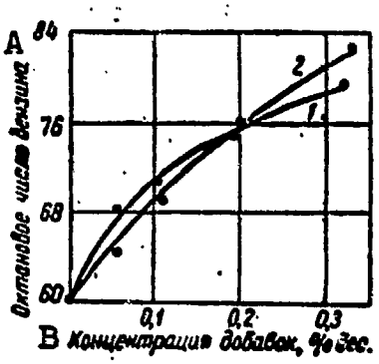



Fig. 133. Effectiveness of ferrocene and PKZh. 1) Ferrocene; 2) PKZh. A) Octane number of gasoline; B) concentration of additives, % by weight.

Another iron antiknock agent that was widely tested in the nineteen-fifties is dicyclopentadienyl iron $Fe(C_5H_5)_2$, which is also known as ferrocene. Ferrocene was first synthesized in 1951 [19, 22-23].

Ferrocene is a yellow crystalline substance having a melting point of 174° and a boiling point of 249°; it begins to distill over 100°; thermally, it is highly stable: its vapors do not decompose on heating to 470°.

Ferrocene has good solubility in hydrocarbons and produces stable gasoline solutions; it is nontoxic [20].

One of the industrial methods of producing ferrocene is that based on the reaction of ferrous chloride with cyclopentadiene in the presence of substances that combine the hydrogen chloride that is liberated in this process (diethylamine, sodium ethylate) [20, 21].

As an antiknock agent, ferrocene is weaker than TES and approximately equivalent to PKZh (Fig. 133); unlike the latter, it has the ability to raise the octane numbers of even ethylated gasolines.

On addition of 0.15% by weight of ferrocene to a direct-distilled gasoline from Tuymazyy petroleum, the octane number of the gasoline was raised from 46 to 61 [23]; the presence of sulfur compounds in the gasoline has virtually no influence on the "receptivity" of the gasoline to ferrocene [24].

However, there is little prospect of practical application for ferrocene, since, like pentacarbonyl iron, it forms ferric oxide on

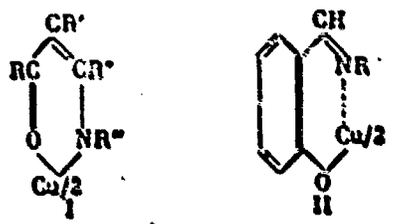
combustion; this oxide is deposited in the engine and shortens its service life [20, 24].

Ferrocene may be used as an antiscaling additive for jet fuels and as an additive to fuels for kerosene lamps, increasing their candle power without increasing the amount of smoke formed.

INTRACOMPLEX COPPER COMPOUNDS

The metal-organic compounds of certain metals, including copper, that possess adequate solubility in gasoline and are stable against oxidation may be produced only in the form of the so-called intracomplex compounds.

Cyclic compounds in which the metal is linked with one terminal group by an ionic bond and with the other by a coordination bond are also known as intracomplex compounds; examples are derivatives of aminomethylene ketones (I), salicylalimines (II), acylamidines, and the like:




The antiknock properties of intracomplex copper salts were discovered in Holland and investigated in many countries from 1931-1942 [10-12].

Intracomplex salts of copper are characterized by rather high antiknock effectiveness. On addition to automotive gasoline with an octane number of 54.8, compounds of type I in concentrations corresponding to a content of 0.1% of copper in the gasoline, the octane number is raised to 64.6.

However, the patents indicate [12] that type I compounds are nevertheless unstable in storage; to prevent formation of deposits, it is

recommended that stabilizers – aromatic amines in concentrations of 5-10% – be added to them.

The problem of the possibility of "scavenging" copper from the engine's combustion chamber is not elucidated in the literature. It is known [13] that the introduction of even traces of copper salts into gasolines sharply accelerates their oxidation. Consequently, gasolines containing 0.1% of copper tar quite rapidly during storage and may form tarry deposits in the engine's induction system. Intracomplex copper salts have not come into practical use.

MANGANESE METHYLCYCLOPENTADIENYL TRICARBONYL (MD-CMT OR AK-33X)

In 1957, the firm "Ethyl Corporation" (USA) patented a new type of antiknock compound – cyclopentadienyl tricarbonyl compounds of manganese having the general formula $AMn(CO)_3$; the cyclopentadienyl group A may contain from 5 to 17 carbon atoms.

TABLE 89

Physical Properties of Cyclopentadienyl Tricarbonyl Compounds of Manganese [34]

| 1 Свойства | 2 Циклопентадиенилтрикарбонил марганца | 3 Метилциклопентадиенилтрикарбонил марганца (АК-33х) |
|---|---|---|
| 4 Плотность | — | 1.39 |
| 5 Температура плавления, °С | 77 | 1.5 |
| 6 Температура кипения, °С | — | 233 |

1) Property; 2) cyclopentadienyl tricarbonyl manganese; 3) methylcyclopentadienyl tricarbonyl manganese (AK-33X); 4) density; 5) melting point, °C; 6) boiling point, °C.

The requirements set forth for antiknock compounds as regards their complex of physicochemical properties (Table 89) is most fully satisfied by manganese methylcyclopentadienyl tricarbonyl $CH_3 \cdot C_5H_4Mn(CO)_3$, which was designated AK-33X and is also known by the

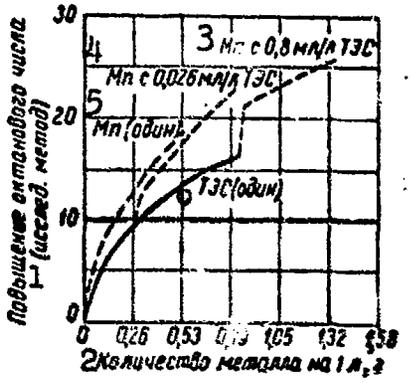



Fig. 134. Increase in octane number of gasoline on addition of TES and AK-33X. 1) Octane-number increase (research method); 2) quantity of metal per 1 liter, g; 3) Mn with 0.8 ml/liter of TES; 4) Mn with 0.026 ml/liter of TES; 5) Mn (alone); 6) TES (alone).

abbreviation MD-CMT (methyl derivative of cyclopentadienyl manganese tricarbonyl [42]).

Manganese cyclopentadienyl tricarbonyl is a solid, while AK-33X is a low-viscosity amber liquid; AK-33X is not soluble in water, dissolves readily in organic solvents at room temperature, and is stable to the action of air and light. The raw materials for production of AK-33X are methylcyclopentadiene, manganous chloride and carbon monoxide. AK-33X is superior to TES (Fig. 134) [34, 35] as regards its effectiveness (on comparison in concentrations by weight) by a factor of approximately 2 if the octane numbers of the gasolines are determined by the research method; the increase in the octane numbers of gasolines as determined by the motor method is approximately the same for both antiknock agents. Increasing the concentration of AK-33X in the gasoline to more than 0.5 g/liter is no longer effective.

The AK-33X antiknock agent raises even the octane number of ethylated gasoline; this is one of its remarkable properties (Fig. 134). The different groups of hydrocarbons array themselves in the same order of receptiveness to AK-33X additives as for TES additives; specifically, the paraffins and naphthenes have the highest receptiveness, while the aromatics respond much more poorly; the receptivity of the olefins varies over a very wide range as a function of their structure. Figure 135 shows the increase in the octane numbers of individual hydrocarbons that already contain TES (0.8 ml/liter) on additional intro-

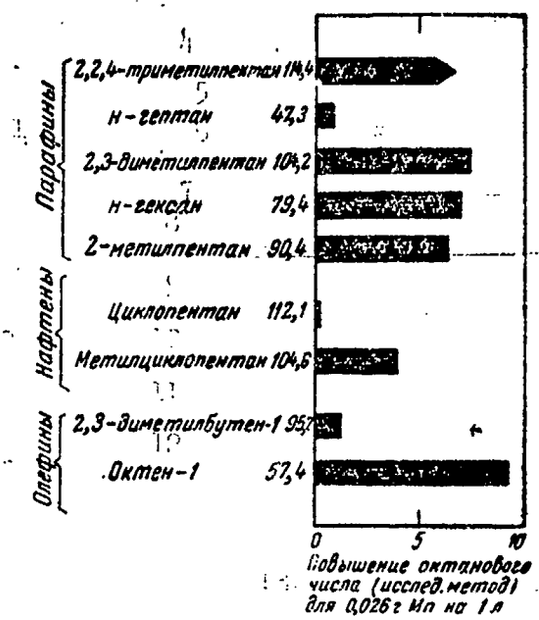



Fig. 135. Octane-number increase in hydrocarbons containing 0.8 ml/liter of TES on addition of AK-33X. 1) Paraffins; 2) naphthenes; 3) olefins; 4) 2,2,4-trimethylpentane; 5) n-heptane; 6) 2,3-dimethylpentane; 7) n-hexane; 8) 2-methylpentane; 9) cyclopentane; 10) methylcyclopentane; 11) 2,3-dimethylbutene-1; 12) octene-1; 13) increase in octane number (research method) for 0.026 g of Mn per 1 liter.

duction of the manganese antiknock agent.

Despite its high effectiveness, the AK-33X antidetonator is regarded [34-36] only as an additive that must be used in combination with TES to raise the octane numbers of ethylated gasolines by a few points, since the cost of the new antidetonator is 2-4 times that of TES [35]. The maximum admissible TES concentration in automotive gasolines is 0.8 ml/liter in the USA; addition of the AK-33X antiknock agent in a concentration of 0.033-0.265 g of Mn per 1 liter of gasoline gets a 1 - 6 point increase (Table 90) in the (research) octane numbers of commercial gasolines. The ethylated components of automotive gasolines – reformed gasoline and the isomerized $C_5$-$C_6$ fraction – have, respectively, lower and higher "receptivity" to AK-33X additives than do commercial gasolines.

Ethylated automotive gasolines containing AK-33X additives were put through extensive bench and road tests [35, 42]. An engine operates no worse on a gasoline with AK-33X than on a gasoline with TES as regards wear, scaling, frequency of surface ignition, and so forth. Halogen compounds may be used as "scavengers" for manganese antiknock agents [42].

Tests of manganese-based antiknock agents are being conducted ...

TABLE 90

Increase in Octane Numbers (Research Method) of Ethylated Gasolines on Addition of AK-33X Antiknock Agent [35]

| 1 Бензины | 2 О. ч. при содержании ТЭС, г/л | 3 Повышение о. ч. при содержании АК-33х, г Mn на 1 л бензина | |
|---|---|---|---|
| | | 0,033 | 0,265 |
| 4 Бензин прямой перегонки: | | | |
| 5 образец В | 84,3 | 2,2 | 4,2 |
| 6 образец Е | 89,1 | 3,2 | 5,1 |
| 7 Риформинг-бензин | 98,8 | 0,3 | 0,3 |
| 8 Изомеризованная фракция $C_5$—$C_6$ | 96,8 | 4,6 | 5,8 |
| 9 Обычный товарный бензин | 93,6 | 1,6 | 2,2 |
| 10 Премиальный товарный бензин | 100,1 | 1,2 | 1,5 |

1) Gasoline; 2) octane number at TES content of, g/liter; 3) rise in octane number with content of AK-33X, g of Mn per 1 liter of gasoline; 4) direct-distilled gasoline; 5) specimen B; 6) specimen E; 7) reformed gasoline; 8) isomerized $C_5$-$C_6$ fraction; 9) ordinary commercial gasoline; 10) premium commercial gasoline.

increasingly wider scales. It is possible that the manganese antiknock agent will ultimately be the optimal antiknock agent, surpassing TES in a number of properties – an agent that has been sought in vain for decades.

ORGANIC ANTIKNOCK ADDITIVES

The organic antiknock additives include certain nitrogen compounds (specifically, aromatic amines), and certain esters; antiknock properties have also been detected in organic compounds of other classes (for example, in naphthalene homologs and others [8, 9]).

The antiknock properties of aromatic amines were discovered in 1919, i.e., before those of TES. Since that time, over 100 patents have been processed for the use of aromatic amines as antiknock additives to gasolines [37].

Phenylenediamines and aniline derivatives with substituents at-

tached either directly to the benzene ring or through the nitrogen of the amino group have been investigated. The relative effectiveness of certain aniline derivatives are given in Table 91.

A special property of the aromatic amines as antiknock agents is their ability to secure a further increase in the antiknock properties of gasolines that already contain TES (Table 92).

As will be seen from Table 92, the use of monomethylaniline (3%) makes it possible to reduce the amount of isooctane by a considerable quantity in the production of high-octane-rating gasolines (from 85.5 to 59.0% for 100-octane gasoline). Aromatic amines are particularly effective in raising the rich-mixture performance numbers of paraffin-base gasolines (Fig. 136).

TABLE 91

Relative Effectiveness of Aniline Derivatives* [37]

| 1 Соединения | 2 Формула | 3 Относительная эффективность |
|---|---|---|
| 4 Анилин | $C_6H_5 \cdot NH_2$ | 0,8 |
| 5 о-Толуидин | $CH_3C_6H_4 \cdot NH_2$ | 0,9 |
| 6 2,6-диметиланилин | $(CH_3)_2 \cdot C_6H_3 \cdot NH_2$ | 1,1 |
| 7 о-Этиланилин | $C_2H_5 \cdot C_6H_4 \cdot NH_2$ | 0,5 |
| 8 2,6-диэтиланилин | $(C_2H_5)_2 \cdot C_6H_3 \cdot NH_2$ | 0,3 |
| 9 N-метиланилин | $C_6H_5 \cdot NH \cdot CH_3$ | 1,0 |
| 10 N-метил-о-толуидин | $CH_3C_6H_4 \cdot NHCH_3$ | 0,6 |
| 11 N-метил-2,6-диметиланилин | $(CH_3)_2C_6H_3 \cdot NH \cdot CH_3$ | 0,2 |

*The effectiveness of N-methylaniline is taken as 1.0.

1) Compound; 2) formula; 3) relative effectiveness; 4) aniline; 5) o-toluidine; 6) 2,6-dimethylaniline; 7) o-ethylaniline; 8) 2,6-diethylaniline; 9) N-methylaniline; 10) N-methyl-o-toluidine; 11) N-methyl-2,6-dimethylaniline.

Technical xylidine and "ekstralin," which is technical monomethylaniline, have been used in practice as antiknock additives.

During the Second World War, xylidine was added in a quantity o.

TABLE 92

Increase in Octane Number of Gasoline Containing 0.05% of TES on Addition of 3% of Monomethylaniline [39]

| 1 Состав бензина, % объемн. | | 2 О. ч. бензина, исследовательский метод | |
|---|---|---|---|
| 3 бензиновый компонент | 4 Изооктан | 5 без ММА | 6 с 3% ММА |
| 64,0 | 36,0 | 80,8 | 92,4 |
| 41,0 | 59,0 | 90,0 | 99,5 |
| 29,0 | 71,0 | 95,0 | >100 |
| 14,5 | 85,5 | 100,0 | >100 |

1) Composition of gasoline, % by volume; 2) octane number of gasoline, research method; 3) gasoline component; 4) isooctane; 5) without MMA; 6) with 3% MMA.

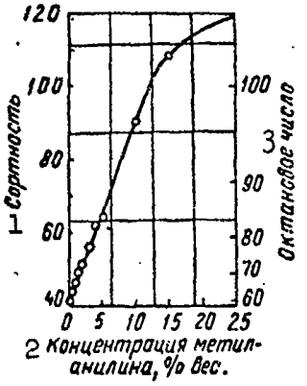



Fig. 136. Increase in octane and performance numbers of fuel with octane number of 60 due to addition of methylaniline. 1) Performance number; 2) concentration of methylaniline, % by weight; 3) octane number.

2% to ethylated aviation gasolines used by the Americans and British [18] to economize on the high-octane components.

Technical xylidine is a liquid having a specific gravity of 0.970-0.990 at 15°, and boiling in the range from 210-221°. The clouding temperature of a 2% solution of technical xylidine in isooctane is about -50°C.

The "ekstralin" additive was developed in the USSR and added to aviation gasolines in quantities of 4% (by weight).

Ekstralin is a colorless liquid of specific gravity $d_4^{20}$ no lower than 0.980 which boils below 195° (97%) and has a freezing point below -55°.

The special properties of aromatic amines as gasoline additives are the lack of "sensitivity" to sulfur compounds, plus their distinct antioxidant properties; aromatic amines inhibit tarring and decomposi-

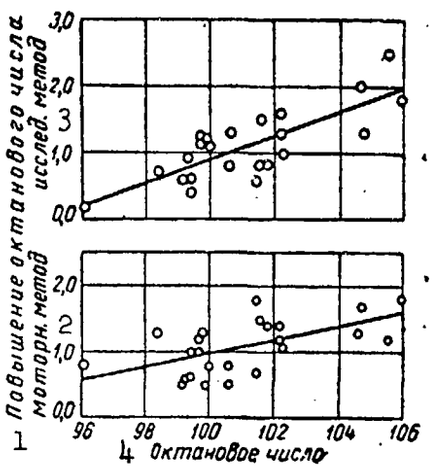



Fig. 137. Increase in octane numbers of 24 specimens of gasolines containing 0.8 ml/liter of TES on addition of 0.75% by volume of TLA. 1) Octane-number increase; 2) motor method; 3) research method; 4) octane number.

tion of TES in gasolines [39].

Apart from the aromatic amines, certain other nitrogen compounds possess antidetonation properties; these include certain homologs of pyridine (for example, the nitrogen bases of shale gasoline and light fractions of coal tars [40, 26], as well as N-substituted aminophenols – methyl-p-aminophenol, monoisopropylaminophenol and others [18].

Toxic oxides of nitrogen form on combustion of the nitrogen compounds.

Certain esters – methyl-tert-butyl ester and ethyl acetate [18] have also been investigated as antiknock agents, and reports appeared in 1959 on a new antiknock additive known as TLA (Texaco Lead Appreciator) [40, 41]. This additive is the organic ester tert-butyl acetate $CH_3$-$COOC_4H_9$, and is a colorless liquid having a specific gravity of 0.886 at 20°; its crystallization temperature is below -60°, and its boiling point is 96.1°. This ester is readily soluble in hydrocarbons, very slightly soluble in water (0.62% at 27°). It is produced from acetic acid and isobutylene. A special property of TLA is the fact that it is effective only on addition to ethylated gasolines; as the TES concentration rises, the effect gained by adding TLA is also enhanced. The optimum TLA concentration in ethylated gasoline is 0.75%. The higher the octane number of the gasoline, the more significant will be the influence of TLA additives in raising its antiknock properties (Fig. 137). It appears that TLA will be used in the USA as an additive to premium (100-octane) automotive gasolines [sic]

will permit raising the gasoline's octane number by 1-2 additional points.

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460 On decomposition, compounds containing 3 and more halogen atoms in the molecule form free halogen [28].

## Chapter 16

### FUELS FOR RECIPROCATING AVIATION ENGINES

During the post-War years, jet aviation engines began to displace reciprocating types, so that the development and perfection of the latter came almost to a halt. But simultaneously helicopters came into considerably more extensive use. At the present time, only helicopters and certain types of airplanes (e.g., transport airplanes) can be listed as aircraft for which reciprocating engines remain the basic type used.

Concurrently with the development of piston engines during the pre-War years and during the Second World War, work was underway toward higher antiknock properties in aviation gasolines. High-quality aviation gasolines such as 100/130 and 115/145 were created.

At the end of the nineteen-forties, research work was underway towards the creation of aviation gasolines based on tryptane and neohexane, which have antiknock properties higher than those of 115/145 gasoline. However, there was no longer any necessity of completing these studies.

The basic grades of aviation gasolines that existed at the end of the War have been retained to the present day; during the post-War period, their qualitative characteristics have undergone only minor changes.

The proportion of aviation gasolines in the over-all balance of aviation-fuel production was reduced considerably by the sharp increase in the production of jet fuels. However, there was no reduc-

tion in the absolute quantity of aviation gasolines processed. In the USA, for example, the total volume of aviation-gasoline production has even increased slightly as compared with the years immediately following the War – to approximately 8-10 million tons per year.

Here, the proportion of aviation gasolines with octane numbers above 100 in the aviation-gasoline production of the USA amounts to about 80% [2].

## REQUIREMENTS SET FORTH FOR QUALITY OF AVIATION GASOLINES

The aviation gasolines used as fuels for reciprocating-type aviation engines must guarantee normal operation of these engines in all modes and under the most severe operational conditions. Consequently, their quality is subject to regulations based on a number of physicochemical indices, which must possess strictly defined values.

The basic quality specifications set forth for contemporary aviation gasolines are as follows.

1. Each grade of aviation gasoline must have certain antiknock properties in both lean and rich mixtures with air. The octane-number and performance number requirements are established at levels such that the aviation gasolines will be able to guarantee normal operation of the engines under the most highly stressed conditions.

Aviation gasolines may not contain more than 2.7-3.3 g of TES/kg of gasoline, depending on the grade of the gasoline. The TES content is limited because it may influence the service life of the engine.

2. Aviation gasolines must possess excellent vaporizability. The fractional composition and saturation vapor pressures of aviation gasolines must guarantee easy starting of the engine at low temperatures (but may not create any danger of vapor-lock formation), and must ensure stable operation of the engine and good performance of it when the operating mode is changed, as well as completeness

porization in the cylinders.

It has been established as a result of numerous tests with aviation engines that the optimum fractional composition of aviation gasolines should be as follows: 10% boiling out no higher than 75-88°, 50% no higher than 105°, 90% no higher than 145° and 97.5% not above 180°.

The saturation vapor pressure should be no higher than 360 mm Hg; during the autumn and winter periods, the lower limit of saturation vapor pressure is also checked; it should not fall lower than 220-240 mm Hg.

3. Aviation gasolines must possess high chemical stability, i.e., they must not form deposits during storage, nor tarry sludges in the fuel-line system, nor scale in the engine's combustion chamber.

To ensure high chemical stability in aviation gasolines, the values of the iodine number (not above 10-12 g/100 g of gasoline) and actual tar content (not above 2 mg/100 ml of gasoline) are restricted; to prevent decomposition of the TES and formation of deposits, addition of antioxidants to aviation gasolines has been made mandatory.

4. Aviation gasolines must possess good low-temperature properties, i.e., they should not deposit paraffin crystals at low temperatures and should not permit formation of ice crystals. For this purpose, the initial-crystallization temperature is established no higher than -60° in aviation gasolines, and the aromatic-hydrocarbon content is restricted, since these compounds possess the highest hygroscopicity.

5. Aviation gasolines must be chemically neutral and may not corrode the metals of tanks, pumping machinery, and engines; the combustion products of aviation gasolines may not corrode the engine components. For this reason, the sulfur content is limited in aviation

gasolines (not over 0.05%), and measures are taken to eliminate active sulfur compounds (negative reaction in copper-plate corrosion test) and water-soluble acids, alkalis and water.

6. Each grade of aviation gasoline must have its own color, so that they can be distinguished readily.

GRADES OF AVIATION GASOLINES

Right up to the Second World War, we used only direct-distillation gasolines as our basic aviation fuels. With the development of reciprocating aviation engines and the petroleum industry's mastery of new production processes, the quality of the aviation gasolines rose continuously; the grades of aviation gasolines being produced also changed accordingly.

The headlong development of aviation-engine design during the Second World War necessitated further improvements to aviation gasolines as regards their antiknock properties.

These requirements were met by the wider use of high-octane components (chiefly isoparaffins), as well as by increasing the concentration of ethyl fluid from 3 to 4 ml/kg (GOST 1012-54).

It was subsequently found that it was not sufficient to characterize the antiknock properties of aviation gasolines in terms of octane number alone. It was established that the performance number of aviation gasolines is of no lesser importance.

The octane number characterizes the antiknock stability of gasolines in lean mixtures, on which the engine operates when it is cruising. Performance number characterizes the detonation stability of a gasoline for rich mixtures, on which the engine is operating in the maximum-power or takeoff modes. Consequently, gasolines having high octane numbers but not possessing adequate performance number cannot guarantee proper operation of an engine during takeoff.

The aromatic components of aviation gasolines of the alkylbenzene type have extremely high performance number and rather high octane number. The question of the use of such hydrocarbons as aviation-gasoline components was first raised by Soviet scientists as long ago as 1936 [3].

Beginning in 1946, aviation gasolines produced by the [Soviet] petroleum industry (GOST 1012-46) have been rated by octane number and performance number as the two most important indices for quality in aviation gasolines.

According to GOST 1012-54, which is still effective, the grades produced are B-100/130, B-95/130, B-91/115 and B-70; there is also a standard for type BA aviation gasoline, which is equivalent to the American 115/145 gasoline (Table 93).

Contemporary aviation gasolines are mixtures of several components. Direct-distillation gasolines from select petroleums and catalytic-cracking gasolines are employed as the base gasolines, which are the main components of commercial aviation gasolines. To obtain the required antiknock properties, isoparaffinic and aromatic components are added to the base gasolines. Except for aviation gasoline B-70, all other grades of aviation gasolines contain ethyl fluid.

GOST 1012-54 makes mandatory the addition of antioxidants to all ethylated [leaded] aviation gasolines to prevent the tetraethyl lead from decomposing while the gasoline is in storage. p-hydroxydiphenylamine is added to ethylated gasolines as an antioxidant in a concentration of 0.004-0.005% (by weight). Consequently, the antioxidant is one of the basic components of contemporary aviation gasolines.

B-100/130 aviation gasoline is produced by mixing catalytic-cracking gasoline with high-quality components. Both catalytic-cracking gasolines and direct-distillation gasolines may serve as base gas-

olines for B-95/130 aviation gasoline. Direct-distillation gasolines serve as the base gasolines in production of B-91/115 and B-70 aviation gasolines.

When p-hydroxydiphenylamine is dissolved in unethylated aviation gasolines, the latter become yellow. When p-hydroxydiphenylamine and lead ethyl fluid are added to a gasoline, it becomes bright orange (B-100/130 gasoline); when orange ethyl fluid is added, the resulting gasoline is yellow (B-95/130), and when blue ethyl fluid is used the resulting color is green (B-91/115).

Recently, a number of quality specifications for aviation gasolines have been refined and formulated more succinctly than previously. For example, it was found that the content of aromatic hydrocarbons in aviation gasolines must be limited. There are two basic reasons for this: 1) the content of aromatic hydrocarbons in a fuel influences the temperature regime of the engine; 2) with increasing aromatic-hydrocarbon content in the gasoline, the engine temperature also rises, and this may shorten its service life.

An elevated content of aromatic hydrocarbons in aviation gasolines is also undesirable from the standpoint of their influence on the hygroscopicity of the gasoline. The solubility of water in aromatic hydrocarbons is considerably higher than its solubility in paraffinic and naphthenic hydrocarbons; benzene is especially hygroscopic. Depending on chemical composition and temperature, aviation gasolines may contain from 0.002 to 0.01% of dissolved water. The danger presented by the presence of hygroscopic water in a fuel consists in the fact that as the temperature and humidity of the air vary during the winter operations period, this water may be precipitated in the form of ice crystals, which may plug the fuel filter and reduce or even cut off the supply of fuel to the engine's cylinders.

TABLE 93

Basic Indices of Aviation-Gasoline Quality

| 1 Физико-химические свойства | ГОСТ 5760-51 (2) | ГОСТ 1012-54 | | | |
|---|---|---|---|---|---|
| | 3 БА | Б-100/130 | Б-95/130 | Б-91/115 | Б-70 |
| 4 Содержание тетраэтилсвинца в *г/кг* бензина не более | 2,7 | 2,7 | 3,3 | 2,5 | — |
| 5 Детонационная стойкость: | | | | | |
| аа) октановое число по моторному методу не менее | — | 98,6 | 95,0 | 91,0 | 70,0 |
| бб) октановое число по температурному методу не менее | — | 100 | — | — | — |
| вв) сортность на бедной смеси не менее | 115 | — | — | — | — |
| dr) сортность на богатой смеси не менее | 160 | 130 | 130 | 115 | — |
| 6 Теплота сгорания низшая в *ккал/кг* не менее | 10 400 | 10 300 | 10 300 | 10 300 | — |
| 7 Фракционный состав: | | | | | |
| аа) температура начала перегонки в °С не выше | 40 | 40 | 40 | 40 | 40 |
| бб) 10% перегоняется при температуре в °С не выше | 75 | 75 | 82 | 82 | 88 |
| вв) 50% перегоняется при температуре в °С не выше | 105 | 105 | 105 | 105 | 105 |
| dr) 90% перегоняется при температуре в °С не выше | 145 | 145 | 145 | 145 | 145 |
| ед) 97,5% перегоняется при температуре в °С не выше | 180 | 180 | 180 | 180 | 180 |
| 8 Давление насыщенных паров, *мм* рт. ст.: | | | | | |
| 9 не менее | 240 | 240 | 220 | 220 | — |
| 10 не более | 360 | 360 | 360 | 360 | 360 |
| 11 Кислотность в *мг* КОН (22) на 100 *мл* бензина 10 не более | 1,2 | 1 | 1 | 1 | 1 |
| 12 Температура начала кристаллизации в °С не выше | —60 | —60 | —60 | —60 | —60 |
| Йодное число в *г*/100 *г* 13 бензина не более | 6 | 12 | 12 | 10 | 10 |
| 14 Содержание фактических смол в *мг*/100 *мл* бензина не более | 2 | 2 | 2 | 2 | 2 |
| 15 Содержание серы в % не более | 0,05 | 0,05 | 0,05 | 0,05 | 0,05 |
| Цвет 16 | В зависимости от цвета этиловой жидкости 17 | Ярко-оранжевый 18 | Желтый 19 | Зеленый 20 | Бесцветный 21 |

[Key on following page]

[Key to Table 93]: 1) Physicochemical property; 2) GOST; 3) BA; 4) content of tetraethyl lead in g/kg of gasoline not above; 5) detonation stability; 5a) motor octane number not below; 5b) temperature-method octane number not below; 5c) lean-mixture performance number not below; 5d) rich-mixture performance number not below; 6) lower-limit heat of combustion in kcal/kg no less than; 7) fractional composition; 7a) initial distillation temperature in °C not above; 7b) 10% distilled at temperature in °C not above; 7c) 50% distilled at temperature in °C not above; 7d) 90% distilled at temperature in °C not above; 7e) 97.5% distilled at temperature in °C not above; 8) saturation vapor pressure, mm Hg; 9) not below; 10) not above; 11) acidity in mg of KOH; 12) initial-crystallization temperature in °C not above; 13) iodine number in g/100 g of gasoline, not above; 14) actual tars content in mg/100 ml of gasoline not above; 15) sulfur content in %, not above; 16) color; 17) depends on color of ethyl fluid; 18) bright orange; 19) yellow; 20) green; 21) colorless; 22) for 100 ml of gasoline.

Addition of aromatic components (toluene, alkylbenzene, pyrobenzene) in an amount totaling no more than 20% to direct-distilled gasolines is permitted for purposes of limiting the aromatic-hydrocarbon content in aviation gasolines. Here, the total content of aromatic hydrocarbons in B-70 aviation gasoline may not exceed 20%.

Also introduced into the GOST for the first time is a quality tolerance as regards fractional composition for aviation gasolines to be stored for long periods (longer than 6 months); since an insignificant variation in fractional composition is not reflected in engine performance, deviations of 1-2° are permitted for such aviation gasolines with respect to the 10%, 50% and 90% distillation points.

Each grade of aviation gasoline must be used in those aviation engines for which it was intended. However, should the basic gasoline grade not be available, aviation engines may also be operated on lower grades of aviation gasoline, but then the engines may not be operated at maximum power. The output restrictions for the engines when a substitute is used for the basic gasoline grade are usually indicated in the special instructions.

Five grades of aviation gasoline are produced in the USA; these are designated 80-84, 91-98, 100-130, 108-135 and 115-145 gasolines.

As will be evident from the list of grades, the USA produces two aviation-gasoline grades with antiknock properties higher than those of 100-130 aviation gasoline. The physicochemical properties of domestic and American aviation gasolines are quite similar. However, the TES content in American gasolines is somewhat lower – about 1.2-2.8 g per 1 kg of gasoline as against 2.5-3.3 g per 1 kg of gasoline in the domestic fuels. The American standard for aviation gasoline provides for checks of the chemical stability of the fuels.

For this purpose, a sample of the gasoline is subjected to 5 hours of "aging" in a stainless-steel bomb at a temperature of 100° and an oxygen pressure of 7 atmospheres. The quantity of deposit after the 5-hour "aging" period may not exceed 6 mg/100 ml of gasoline; the quantity of lead compounds in the deposit may not be greater than 3 mg. So that the gasoline will be able to meet these requirements, antioxidants are added to it in amounts equal to 0.0015-0.003% by weight.

The antioxidants used are N,N'-di-sec-butyl-p-phenylenediamine, 2,4-dimethyl-6-tert-butylphenol and 2,6-di-tert-butyl-4-methylphenol. These antioxidants may be added to gasolines either separately or in mixtures with one another.

INCREASING STABILITY OF ETHYLATED GASOLINES IN STORAGE

One of the basic problems dealt with in the postwar years was that of raising the stability of aviation gasolines for storage. To solve this problem, extensive investigations were carried out in the USSR and abroad [5, 6, 7].

It was found that ethylated aviation gasolines possess inadequate stability and readily form precipitates consisting 40-45% of lead [4, 5, 6] on oxidation at normal temperatures.

Such deposits form particularly rapidly when aviation gasolines

are stored in the southern climatic zone. Under the climatic conditions of the southern USSR, decomposition products of TES form deposits even after 2-3 months of storage in small tanks (volumes less than 50 $m^3$) or even faster. Aviation gasolines could be stored no longer than 1-1.5 years even in large underground and surface tanks, and this presented an obstacle to accumulation of reserve supplies.

When the deposits got into the engine, they plugged fuel filters, upset the normal performance of the aviation spark plugs and caused airplane crashes.

In this connection, studies were made to determine the liquid-phase oxidizability of the individual gasoline hydrocarbons with 7 to 10 carbon atoms and the influence of TES on oxidation of these hydrocarbons [8] (Table 94). The TES was added to the hydrocarbons in its normal concentration (about 0.1 mole-%). It was established that the relationships observed in oxidation of oil hydrocarbons [9] may also be extended to the hydrocarbons that form gasolines. For example, normal paraffinic hydrocarbons and hydrocarbons with the iso-structure containing a quaternary carbon atom were much more stable without TES against liquid-phase oxidation than the hydrocarbons of other groups.

Paraffinic-hydrocarbons with "unprotected" tertiary C-H bonds oxidize considerably more easily than naphthenic and aromatic hydrocarbons. However, unlike the hydrocarbons with higher molecular weights, monocyclic naphthenic hydrocarbons with short side chains are more resistant to oxidation in the absence of TES than the corresponding aromatic hydrocarbons. Five-member naphthenes are particularly resistant to liquid-phase oxidation; their oxidation-induction periods are considerably longer than those of the six-member naphthenes of corresponding molecular weight (Table 94).

TES reduces the oxidation-induction periods of hydrocarbons, in-

creases their oxidation rate and, undergoing oxidation itself, forms deposits. No more than 10% of the combined oxygen is expended in oxidizing it.

TES influences to different degrees the oxidizability of hydrocarbons that oxidize at practically the same rate in the absence of TES (cf. n-heptane, 2,2,4-trimethylpentane and toluene in Table 94).

The paraffinic (with the exception of hydrocarbons having "unprotected" tertiary C-H bonds) and naphthenic hydrocarbons show, after addition of TES, longer stability periods than aromatic hydrocarbons and olefinic hydrocarbons; trimethylpentanes, which contain a quaternary carbon atom in the molecule, are distinguished by high stability.

Decomposition of TES in a solution of olefinic hydrocarbons takes place at low speed despite the fact that olefinic hydrocarbons oxidize more intensively (Table 94).

The influence of hydrocarbon hydroperoxides on the decomposition of TES was investigated to explain the mechanism by which TES acts in the process of liquid-phase hydrocarbon oxidation [10]. It was shown that hydroperoxides of differing structure are characterized by different "activities" with respect to TES (Fig. 138). When mixed hydrogen peroxides of $C_8$ olefins ("hyperol") were added to a hydrocarbon containing TES, oxygen was absorbed by the hydrocarbon at a higher rate than on addition of isopropylbenzene hydroperoxide (Fig. 138a, curves 1 and 2), while the rate of decomposition of TES, on the other hand, was smaller in the presence of the hydroperoxides of olefinic hydrocarbons (Fig. 138b). It is appropriate to compare this result with the data of Table 94, from which it is evident that decomposition of TES in a solution of olefinic hydrocarbons also takes place at a speed considerably lower than in solutions of hydrocarbons of other

TABLE 94

Characterization of Hydrocarbon Oxidizabilities in the Liquid Phase ($t = 100°C$; $p_0 = 1$ atmosphere absolute)

Symbols: $\tau$ is the induction period in hours; $w_1$ is the average rate of absorption of oxygen after the induction period in moles/(mole) hour; $w_2$ is the average rate of decomposition of TES after the induction period in moles/(mole) hour; it is computed from the quantity of deposit formed by the TES combustion products.

| 1 Углеводороды | Без этиловой жидкости | | С этиловой жидкостью | | | С этиловой жидкостью + 0,004% *n*-оксидифениламина |
|---|---|---|---|---|---|---|
| | $\tau$ | $w_1 \cdot 10^4$ | $\tau$ | $w_1 \cdot 10^4$ | $w_2 \cdot 10^4$ | |
| *1. Парафиновые углеводороды* | | | | | | |
| *n*-Гептан | ~30 | 0,6 | 5 | 3,6 | 0,7 | 45 |
| *n*-Октан | ~24 | 1,7 | 3 | — | — | 50 |
| *n*-Нонан | ~16 | 1,3 | 4 | — | — | — |
| *n*-Декан | ~16 | 1,1 | 3 | — | — | — |
| 2,2,4-триметилпентан | <40 | 0,3 | 20 | 0,6 | 0,1 | 50 |
| Смесь триметилпентанов 2,2,3—80%, 2,3,3—8%, 2,3,4—12% | ~27 | 1,0 | ~8 | 13,5 | 1,0 | — |
| 2,6-диметилгептан | ~2 | 13,0 | <1 | — | — | — |
| *2. Нафтеновые углеводороды* | | | | | | |
| а) пятичленные: | | | | | | |
| этилциклопентан | ~16 | — | 9 | — | — | 92 |
| *n*-пропилциклопентан | >8 | — | — | — | — | 88 |
| б) шестичленные: | | | | | | |
| метилциклогексан | ~8 | 3,4 | 8 | 6,9 | 1,0 | — |
| этилциклогексан | ~6 | 1,4 | 3 | 25,6 | 1,4 | 29 |
| изопропилциклогексан | <4 | 3,7 | 3 | 21,8 | 1,0 | 33 |
| *3. Ароматические углеводороды* | | | | | | |
| Толуол | ~36 | 0,4 | 3 | 6,7 | 0,7 | 12 |
| Этилбензол | <1 | 3,4 | 1 | 18,4 | 1,0 | 12 |
| Изопропилбензол | <1 | 4,1 | 1 | 17,9 | 1,4 | 14 |
| *4. Фракции, содержащие непредельные углеводороды* | | | | | | |
| Фракция спиртна $C_8$ (содержание непредельных 27,2%) | <1 | 10,5 | <1 | 26,1 | 0,3 | — |
| Фракция спиртна $C_9$ (содержание непредельных 25,4%) | <1 | 35,5 | <1 | 25,5 | 0,3 | 1,5 |
| Смесь октиленов с прямыми цепями | <1 | 59,5 | <1 | — | — | 1,5 |
| Смесь октиленов разветвленного строения (фракция 107—112° диизобутилена) | <1 | 69,2 | <1 | — | — | 2 |

1) Hydrocarbons; 2) without ethyl fluid; 3) with ethyl fluid; 4) with ethyl fluid + 0.004% p-hydroxydiphenylamine; 5) paraffinic hydrocarbons; 6) n-heptane; 7) n-octane; 8) n-nonane; 9) n-decane; 10) 2,2,4-trimethylpentane; 11) trimethylpentane mixtures; 12) 2,6-dimethylheptane; 13) naphthenic hydrocarbons; 14) five-member; 15) ethylcyclopentane; 16) n-propylcyclopentane; 17) six-member; [Key continued on following page]

[Key to Table 94 continued]: 18) methylcyclohexane; 19) ethylcyclohexane; 20) isopropylcyclohexane; 21) aromatic hydrocarbons; 22) toluene; 23) ethylbenzene; 24) isopropylbenzene; 25) fractions containing unsaturated hydrocarbons; 26) $C_8$ synthol fraction (containing 27.2% unsaturated hydrocarbons); 27) $C_9$ synthol fraction (containing 25.4% unsaturated hydrocarbons); 28) mixture of octylenes with straight chains; 29) mixture of branched-structure octylenes (107-112° diisobutylene fraction).

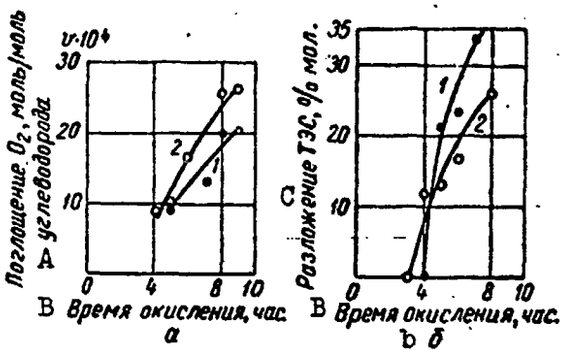


Fig. 138. Influence of peroxides on oxidation of ethylated 2,2,4-trimethylpentane. a) absorption of oxygen; b) decomposition of TES. 1) 2,2,4-trimethylpentane + giperiz [hyperiz] (0.5 mole of peroxide per 1 mole of TES); 2) 2,2,4-trimethylpentane + hyperol (0.5 mole of peroxide per 1 mole of TES). A) Absorption of $O_2$, moles/mole of hydrocarbon; B) oxidation time, hours; C) decomposition of TES, mole-%.

groups.

The characteristics of the mechanism by which TES acts during the presence of liquid-phase oxidation of hydrocarbons consist in the following.

1. At relatively low temperatures, TES decomposes easily to form free radicals that initiate oxidation of the hydrocarbons. It is probable that not only ethyl, but also alkyl-lead radicals form in this process:

$$Pb(C_2H_5)_4 \rightarrow Pb(C_2H_5)_3 + C_2H_5\cdot$$

2. The organic peroxides that form react with the TES and accelerate its decomposition; here, the dialkyl lead compounds $(C_2H_5)_2Pb(OH)_2$, $(C_2H_5)_2Pb(OR)_2$, $(C_2H_5)_2Pb(OR)(OH)$, form together with PbO and settle in the deposit.

3. The peroxides of different hydrocarbons are characterized by differing abilities with respect to TES; this will probably account for the differing degrees to which TES is active in oxidizing hydrocarbons with different structures.

To ascertain the relationship between the hydrocarbon composition of the gasolines and their stability, binary mixtures of easily oxidized and hard-to-oxidize hydrocarbons were oxidized [5]. It was shown that the oxidizability of mixtures of the hydrocarbons that are contained in aviation gasolines is determined to a considerable degree – particularly in the presence of TES – by the content of olefinic hydrocarbons. Even in small concentrations (2-5%), olefins begin to exert a significant influence on oxidation. The stability times of ethylated mixtures of aromatic and isoparaffinic hydrocarbons do not change additively as a function of mixture composition; on addition of 10% of an easily oxidized aromatic hydrocarbon (ethylbenzene) to the hard-to-oxidize 2,2,4-trimethylpentane, its stability period begins to diminish noticeably.

The decomposition process of TES in hydrocarbon solutions may be retarded by the use of antioxidants.

Only antioxidants that produce inactive radicals not only with hydrocarbon radicals but also with the alkyl-lead radicals produced by the TES can be used as antioxidants for ethylated aviation gasolines.

Consequently, antioxidants of phenol type, as well as sulfanilimide compounds and disulfides produce absolutely no inhibition of the decomposition of TES in ethylated aviation gasolines.

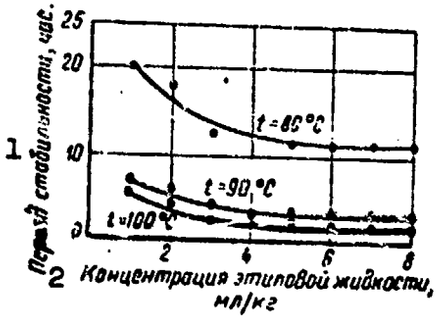


Fig. 139. Stability of ethylated aviation gasoline from direct distillation as a function of TES concentration and temperature. 1) Stability period, hours; 2) ethylfluid concentration, ml/kg.

"Screened" alkylphenols and phenylenediamines are quite effective; even more effective are the aminophenols – benzyl-p-aminophenol and p-hydroxydiphenylamine. It is representatives of these antioxidant groups that have come into practical use for stabilization of aviation gasolines: p-hydroxydiphenylamine in the USSR and 2,6-di-tert-butyl-4-methylphenol, 2,4-dimethyl-tert-butylphenol and N,N'-di-sec-butyl-p-phenylenediamine in the USA.

TABLE 95

Chemical Stability of Ethylated Aviation-Gasoline Components [12]

(Content of TES 0.33% by Weight)

| 1 Бензины | Период стабильности 2 (при 110°С) | |
|---|---|---|
| | 3 без антиокислителя | 4 с 0,004% вес. п-оксидифениламина |
| 5 А. Бакинские бензины прямой гонки | | |
| 6 Сураханский | ~1 | 20 |
| 7 Балаханский | ~1 | 15 |
| 8 Биби-эйбатский | ~1 | 14 |
| 9 В Б. Бензины каталитического крекинга (авиакомпоненты) | | |
| 10 Гурьевский | 1 | 28 |
| 11 Орский | 1 | 32 |
| 12 СВ. Технические алкилбензолы | | |
| 13 Образец № 1 | <0,5 | 6 |
| 14 Образец № 2 | <0,5 | 1 |
| 15 Dг. Технические алкилаты | | |
| 16 Гурьевский | 1,5 | 18 |
| 17 Орский | 1,5 | 21 |

1) Gasoline; 2) stability period (at 110°C); 3) without antioxidant; 4) with 0.004% by weight of p-hydroxydiphenylamine; 5) direct-distillation Baku gasolines; [Key continued on following page]

[Key to Table 95 continued]: 6) Surakhany; 7) Balakhany; 8) Bibi-eybat; 9) catalytic-cracking gasolines (aviation components); 10) Gur'yevskiy; 11) Orsk; 12) technical alkylbenzenes; 13) specimen No. 1; 14) specimen No. 2; 15) technical alkylates; 16) Gur'yevskiy; 17) Orsk.

p-Hydroxydiphenylamine is more effective than the antioxidants widely used in the USA.

When p-hydroxydiphenylamine and ionene are added together to a gasoline, we observe a reciprocal enhancement of the effects of these antioxidants [11].

Unlike the American antioxidants, p-hydroxydiphenylamine has a low solubility in gasolines and is introduced into them in a benzene solution.

Having considered the information given above on the oxidizabilities of individual hydrocarbons and the effectiveness of antioxidants, let us pass to an evaluation of the stabilities of aviation gasolines [12, 13].

Apart from hydrocarbon composition, the stability of aviation gasolines depends on a number of other factors, including the TES concentration in the gasoline: it diminishes as the TES content is increased to a certain limit (to 3-4 ml of ethyl fluid per 1 kg of gasoline); a further increase in TES concentration has practically no further influence (Fig. 139).

The structure of the halogenoalkyls used in the ethyl fluid as a lead "scavenger" does not influence the stability of aviation gasolines.

In the presence of ethyl fluid, the aviation-gasoline components – direct-distilled Baku gasolines on a naphthenic base, catalytic-cracking gasolines and technical alkylates – are rather close together as regards oxidizability (Table 95). Both the alkylbenzenes and the individual aromatic hydrocarbons are characterized by low "recep-

tiveness" to p-hydroxydiphenylamine.

The results of experiments with prolonged storage of gasolines under real conditions in various climatic zones have shown that aviation gasolines stabilized with p-hydroxydiphenylamine can be stored for 3-4 years without losing stability [14].

This storage life is guaranteed by a new indicator introduced into the GOST for domestic aviation gasolines: "stability period not less than 8 hours."

Aviation gasolines in long-term storage should be removed from storage when the stability period has dropped to 2 hours.

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## Chapter 17

## AUTOMOTIVE GASOLINES

Automotive gasolines presently occupy one of the most important places in the manufacture of petroleum products. The production of these gasolines in various countries amounts to 20 to 50% of the total quantity of petroleum products produced.

More than 4/5 of all automobiles operate on carburetor engines, designed to function on automotive gasolines. There is a continuously increasing demand for automotive gasoline as the number of cars in our country increases. By 1975 the multitude of cars in our country will consume twice as much automotive gasoline as in 1965, and 3.3 times as much gasoline as in 1958.

### GRADES OF AUTOMOTIVE GASOLINES

At the present time the All-Union State Standard (GOST 2084-56) provides for the production of four basic brands of automotive gasolines: A-66, A-72, A-74, and A-76 (Table 96).

The A-66 gasoline is produced for the majority of the automotive engines (whose compression ratios do not exceed 6.2-6.3) presently in use. This gasoline is divided into conventional and climatized gasoline. The climatized gasoline is of a lighter fractional composition and is intended for use in the northern regions of the country during the winter. The A-74 gasoline is produced for the engines of ZIL-110 automobiles, and the A-72 and A-76 gasolines must provide for knock-free operation of the new automotive engines which are now being tested, put into production, and are, in part, being produced by the

domestic automotive industry.

Contemporary automotive gasolines are produced at petroleum-refining plants by mixing several components. The base components are the gasolines derived through direct distillation, and through thermal and catalytic cracking. The fraction of a particular component that is used in a commercial gasoline depends on the quality of the component and the over-all balance of light petroleum products produced at the plant. A typical composition of commercial automotive gasolines for some domestic refineries is presented in Table 97.

TABLE 96

Industrial Specifications for Automotive Gasolines

| 1 Физико-химические свойства бензинов | 2 Показатели по маркам | | | | |
|---|---|---|---|---|---|
| | А-66 | | | | |
| | 3 обычный | 4 зимний | А-72 | А-74 | А-76 |
| 5 Детонационная стойкость: | | | | | |
| 6 а) октановое число, определяемое по моторному методу, не менее | 66 | 66 | 72 | 74 | 76 |
| 7 б) октановое число, определяемое по исследовательскому методу, не менее | 27 Не нормируется | | 76 | Не нормируется | 80 |
| 8 Содержание ТЭС в г/кг бензина не более | 0,82 | 0,82 | 28 Отсутствие | | 0,41 |
| 9 Фракционный состав (перегоняется при температуре, °С): | | | | | |
| 10 а) к. к. не ниже | — | — | — | 85 | — |
| 11 б) 10% не выше | 79 | 65 | 75 | 79 | 75 |
| 12 в) 50% не выше | 145 | 120 | 135 | 105 | 135 |
| 13 г) 90% не выше | 185 | 175 | 180 | 165 | 180 |
| 14 д) к. к. не выше | 205 | 190 | 195 | 180 | 195 |
| 15 е) остаток в колбе в % не более | 1,5 | 1,5 | 1,5 | 1,5 | 1,5 |
| 16 ж) остаток и потери в % не более | 4,5 | 4,5 | 3,5 | 2,5 | 3,5 |
| 17 Давление насыщенных паров в мм рт. ст. не более | 500 | 700 | 500 | 500 | 500 |
| 18 Кислотность в мг КОН/100 мл не более | 3 | 3 | 3 | 2 | 3 |
| 19 Содержание фактических смол в мг/100 мл бензина не более: | | | | | |
| 20 а) на месте производства бензина (до этилирования) | 7 | 7 | 5 | 2 | 5 |
| 21 б) на месте потребления бензина | 20 | 20 | 10 | 2 | 10 |
| 22 Индукционный период в мин. не менее | 360 | 360 | 480 | 600 | 480 |
| 23 Содержание серы в % не более | 0,15 | 0,15 | 0,15 | 0,10 | 0,15 |
| 24 Испытание на медной пластинке | 29 Выдерживает | | | | |
| 25 Содержание водорастворимых кислот и щелочей | 30 Отсутствие | | | | |
| 26 Содержание механических примесей и воды | | | | | |

1) Physicochemical properties of gasolines; 2) indicators, by brand; 3) standard; 4) climatized; 5) antiknock sta- [Key continued on following page]

[Key to Table 96 continued]: bility; 6) a) octane number, determined according to the motor method, not less than; 7) b) octane number, determined according to the research method, not less than; 8) TES [TEL-tetraethyllead] content in g/kg of gasoline, not more than; 9) fractional composition (distilled at a temperature, °C); 10) a) start of boiling not below; 11) b) 10% not above; 12) c) 50% not above; 13) d) 90% not above; 14) e) end of boiling not above; 15) f) residue in flask, in %, not more than; 16) g) residue and losses, in %, not more than; 17) pressure of saturated vapors, in mm Hg, not more than; 18) acidity in mg KOH/100 ml, not more than; 19) content of actual tars, in mg/100 ml of gasoline, not more than; 20) a) at point of petroleum production (prior to ethylation); 21) b) at point of gasoline utilization; 22) induction lag, in minutes, not less than; 23) sulfur content, in %, not more than; 24) test on copper plate; 25) content of water-soluble acids and alkalis; 26) content of mechanical admixtures and water; 27) not standardized; 28) absent; 29) withstands; 30) absent.

TABLE 97

Composition of commercial automotive gasolines in terms of components, at certain petroleum refineries [29, etc.]

| 1 Компоненты | 2 Содержание компонентов в товарном бензине по заводам, % | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3 Ново-Уфимский | | 4 Уфимский | 5 Черниговский | 6 Омский | 7 Сызранский | 8 Куйбышевский | 9 Новокуйбышевский | | 10 Красноводский | 11 Бакинский |
| | А-66 | А-72 | А-66 | А-72 | | А-56 | А-66 | А-66 | А-72 | А-66 | А-70 |
| 12 Бензин прямой гонки | 51 | 30 | 73 | — | — | 55 | 56 | 55 | 15 | 47 | 5 |
| 13 Бензин термического крекинга | 34 | — | 27 | — | — | 45 | 27 | 39 | — | 48 | 95 |
| 14 Бензин каталитического крекинга | 13 | 70 | — | — | 55 | — | 17 | 6 | 70 | — | — |
| 15 Бензин каталитического риформинга | — | — | — | 100 | 45 | — | — | 8 | 15 | — | — |
| 16 Продукты переработки углеводородных газов | 2 | — | — | — | — | — | — | 2 | — | 5 | — |

1) Components; 2) content of components in commercial gasoline, by refineries, %; 3) Novo-Ufa; 4) Ufa; 5) Chernigov; 6) Omsk; 7) Syzran'; 8) Kuybyshev; 9) Novokuybyshev; 10) Krasnovodsk; 11) Baku; 12) direct-distillation gasoline; 13) thermal-cracking gasoline; 14) catalytic-cracking gasoline; 15) catalytic-reforming gasoline; 16) products resulting from the refining of hydrocarbon gases.

The A-66 gasoline is basically prepared by mixing two components: direct-distillation and thermal-cracking gasolines. At those refin-

eries which have installations for the refining of hydrocarbon gases, the following products of these processes are used in commercial gasolines – the spent butane-butylene fraction, the pentane-amylene fraction, gaseous gasoline, polymer gasoline, etc.

The A-72 gasoline is prepared on a base of single-stage catalytic-cracking and catalytic-reforming gasolines with the addition of those products obtained by other processes in the refining of petroleum and hydrocarbon gases.

In recent years the petroleum-refining industry has begun the production of the high-quality automotive gasoline "Ekstra" for the ZIL-111 and "Chayka" automobiles. Gasolines produced by catalytic processes, containing admixtures of high-octane components (alkylate, toluene, alkylbenzene, industrial isooctane, isopentane, etc.) are used for the production of the above-mentioned gasoline as well as for export brands.

The techniques involved in the production of the "Ekstra" gasoline have not yet been finalized. It is produced in individual batches, each having a different ratio of components (Table 98).

The "Ekstra" gasoline (batch 3, Table 98) successfully passed all tests in a ZIL-111 engine and is presently used in domestic higher-class automobiles.

In addition to the automotive gasolines for the domestic market, the refineries are producing export gasolines under the brands indicated in Table 99.

Our export gasolines are on a par, from the standpoint of quality, with the best European brands and are in great demand in many countries.

The selection of the automotive-gasoline grade required for normal operation of a given automobile is a function of the structural

TABLE 98

Composition and Properties of Specimens of "Ekstra" Gasoline

| 1 Показатели | 2 Партия 1 | 2 | 3 |
|---|---|---|---|
| 3 Состав по компонентам, % вес.: | | | |
| 4 а) бензин каталитического крекинга | 40,0 | 40,0 | 20,0 |
| 5 б) алкилат | 33,0 | 35,0 | 35,0 |
| 6 в) толуол | 17,8 | 10,0 | 15,0 |
| 7 г) головные фракции бензина прямой гонки | 9,2 | — | — |
| 8 д) газовый бензин | — | 15,0 | 10,0 |
| 9 е) изооктилен | — | — | 10,0 |
| 10 ж) ксилольная фракция гидроформинга | — | — | 10,0 |
| 11 Октановое число по исследовательскому методу: | | | |
| 12 а) в чистом виде | 91,6 | 89,9 | 95,0 |
| 13 б) с добавкой ТЭС | 98,0 | 96,2 | — |
| 14 Содержание ТЭС в *г/кг* бензина | 0,998 | 1,23 | Отс. |
| 15 Фракционный состав (перегоняется при температуре, °С): | | | |
| 16 а) н. к. | 38 | 45 | 36 |
| 17 б) 10% | 58 | 61 | 65 |
| 18 в) 50% | 104 | 105 | 115 |
| 19 г) 90% | 158 | 173 | 146 |
| 20 д) к. к. | 179 | 188 | 167 |
| 21 е) остаток и потери, % | 3,5 | 3,5 | 4,0 |
| 22 Давление насыщенных паров, *мм* рт. ст. | 400 | 327 | 300 |
| 23 Кислотность, *мг* КОН/100 *мл* | 0,26 | 0,01 | 0,13 |
| 24 Содержание фактических смол, *мг*/100 *мл* | 30 1,8 | 4,8 | 1,6 |
| 25 Индукционный период, мин. | Выше 600 | Выше 600 | Выше 600 |
| 26 Содержание серы, % | 0,026 | 0,15 | 0,022 |
| 27 Испытание на медной пластинке | 31 Выдерживает | | |
| 28 Содержание водорастворимых кислот и щелочей | Отсутствие | | |
| 29 Содержание механических примесей и воды | 32 » | | |

1) Indicators; 2) batch; 3) composition by components, % by weight; 4) a) catalytic-cracking gasoline; 5) b) alkylate; 6) c) toluene; 7) d) head fractions of direct-distillation gasoline; 8) e) gaseous gasoline; 9) f) isooctylene; 10) g) hydroforming xylene fractions; 11) octane number, according to research method; 12) a) in pure form; 13) b) with addition of tetraethyllead (TES [TEL]); 14) TES [TEL] content, in g/kg of gasoline; 15) fractional composition (distilled at a temperature of, °C); 16) a) start of boiling; 17) b) 10%; 18) c) 50%; 19) d) 90%; 20) e) end of boiling; 21) f) residue and losses, %; 22) pressure of saturated vapors, mm Hg; 23) acidity, mg KOH/100 ml; 24) content of actual resins, mg/100 ml; 25) induction lag, minutes; 26) sulfur content, %; 27) test on copper plate; 28) content of water-soluble acids and alkalis; 29) content of mechanical impurities and water; 30) above 600; 31) withstands; 32) absent.

features of the particular engine in question. The factory, in its instructions for the automobile, provides special stipulations as to the grade of automotive gasoline with which the particular engine suc-

TABLE 99

Technical Specifications for Export Automotive Gasolines

| 1 Показатели | 2 Нормы по маркам | | | | | | |
|---|---|---|---|---|---|---|---|
| | 74 | 83 | 87 | 90 | 93 | 95 | 98 |
| 3 Плотность $\rho_4^{20}$ не выше | 0,740 | 0,750 | 0,745 | 0,745 | 0,745 | 0,735 | 0,735 |
| 4 Содержание ТЭС в мл/кг не более | 17 отс. | 0,6 | 0,7 | 0,73 | 0,75 | 0,78 | 0,75 |
| 5 Октановое число: | | | | | | | |
| 6 по исследовательскому методу не ниже | — | 83 | 87 | 90 | 93 | 95 | 98 |
| 7 по моторному методу не ниже | 74 | 78 | 83 | 84 | 85 | 86 | 90 |
| 8 Фракционный состав (перегоняется при температуре, °С): | | | | | | | |
| 9 а) 10% не выше | 70 | 75 | 75 | 75 | 70 | 70 | 70 |
| 10 б) 50% не выше | 105 | 120 | 120 | 120 | 120 | 110 | 110 |
| 11 в) 90% не выше | 165 | 180 | 180 | 180 | 180 | 160 | 160 |
| 12 г) к. к. не выше | 180 | 205 | 205 | 205 | 195 | 180 | 180 |
| 13 Давление насыщенных паров в мм рт. ст. не более | 500 | 500 | 500 | 500 | 500 | 450 | 450 |
| 14 Содержание смол в мг/100 мл бензина не более | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| 15 Индукционный период в мин. не менее | 800 | 500 | 500 | 500 | 500 | 500 | 500 |
| 16 Содержание серы в % не более | 0,1 | 0,1 | 0,1 | 0,1 | 0,1 | 0,05 | 0,05 |

1) Indicators; 2) standards for various brands; 3) density $\rho_4^{20}$, not higher than; 4) TES [TEL] content in ml/kg, not more than; 5) octane number; 6) by the research method, not lower than; 7) by the motor method, not lower than; 8) fractional composition (distills at a temperature of, °C); 9) a) 10%, not higher than; 10) b) 50%, not higher than; 11) c) 90%, not higher than; 12) d) end of boiling, not higher than; 13) pressure of saturated vapors in mm Hg, not greater than; 14) content of resins in mg/100 ml of gasoline, not higher than; 15) induction lag in minutes, not less than; 16) sulfur content in %, not more than; 17) absent.

cessfully passed extensive factory tests and which (gasoline) serves as the basic grade of fuel for this engine.

It should be borne in mind that there is no other fuel which completely replaces automotive gasoline. Even aviation gasoline (B-70) does not fully correspond to the requirements of an automotive gasoline. This gasoline exhibits a somewhat higher temperature at which 10% boils off, and therefore the starting properties of this gasoline are inferior to those of automotive gasolines. Repeated

tests have also shown that in operations with B-70 gasoline an automotive engine generally overheats. The latter is, apparently, caused by the lower viscosity of the B-70 gasoline as a result of which a larger quantity of fuel manages to pass through the constant orifice of the carburetor jets and there is formed a combustible mixture that is richer in composition than would be the case with operations on automotive gasoline [2].

Automotive engines designed for low antiknock values of the gasolines used can be employed with automotive-gasoline grades that exhibit higher antiknock properties, but there will be no improvement in engine operation in this case, and the cost of the high-octane gasolines will always be higher than that of the low-octane gasolines.

CHEMICAL COMPOSITION OF AUTOMOTIVE GASOLINES

Automotive gasolines are a complex mixture of various hydrocarbons containing a small quantity of nonhydrocarbon admixtures – sulfur, nitrogen, and oxygen compounds. The chemical composition of commercial automotive gasolines is extremely inconstant and is a function of the quantity and quality of the components. Since commercial automotive gasolines consist primarily of components obtained by direct distillation and by thermal and catalytic cracking, it is natural that the physicochemical and operational properties of these gasolines be determined primarily by the chemical composition of these three components.

The gasolines obtained through the direct distillation of petroleum are the most thoroughly studied components of automotive gasolines. The content of certain hydrocarbons in gasolines produced by direct distillation is wholly dependent on the presence of these hydrocarbons in the initial petroleum. The quantity of aromatic and naphthenic hydrocarbons in these gasolines, as a rule, increases as

TABLE 100

Group Composition of Direct-Distillation and Thermal-Cracking Gasolines Produced from the Same Petroleums

| 1 Бензины | 2 Удельный вес $d_4^{20}$ | 3 Начало кипения, °С | 4 Конец кипения, °С | 5 Групповой состав, % 6 непредельные углеводороды | 7 ароматические углеводороды | 8 нафтеновые углеводороды | 9 парафиновые углеводороды |
|---|---|---|---|---|---|---|---|
| 10 Бакинский прямой гонки | 0,753 | 50 | 188 | 0 | 3,7 | 52,7 | 43,6 |
| 11 Бакинский крекинг-бензин | 0,731 | 29 | 187 | 25,6 | 11,7 | 9,4 | 53,3 |
| 12 Грозненский прямой гонки | 0,723 | 40 | 190 | 0 | 3,0 | 32,3 | 64,7 |
| 13 Грозненский крекинг-бензин | 0,718 | 26 | 188 | 27,6 | 16,4 | 6,2 | 49,8 |

1) Gasolines; 2) specific weight $d_4^{20}$; 3) start of boiling, °C; 4) end of boiling, °C; 5) group composition, %; 6) unsaturated hydrocarbons; 7) aromatic hydrocarbons; 8) naphthenic hydrocarbons; 9) paraffinic hydrocarbons; 10) direct-distillation Baku; 11) Baku cracking gasoline; 12) direct-distillation Groznyy; 13) Groznyy cracking gasoline.

TABLE 101

Content of Hydrocarbon Groups (in %) in Thermal-Cracking Gasoline [3]

| 1 Пределы выкипания фракции, °С | 2 Выход фракции, % от фракции, 60°—200° | 3 Непредельные: 4 циклические: 5 шестичленные | 6 пятичленные | 7 ароматические | 8 ациклические | 9 Ароматические | 10 Гексаметиленовые | 11 Пентаметиленовые | 12 Парафиновые |
|---|---|---|---|---|---|---|---|---|---|
| 60—95 | 18 | 4.6 | 11.8 | — | 34.1 | 4.7 | 5.1 | 5.9 | 33.8 |
| 95—122 | 20 | 7.2 | 16.7 | 1.2 | 24.5 | 9.3 | 10.4 | 6.4 | 21.3 |
| 122—150 | 23 | 8.3 | 13.0 | 2.3 | 21.3 | 13.3 | 8.7 | 7.4 | 25.7 |
| 150—200 | 39 | 8.1 | 9.0 | 1.8 | 21.4 | 13.9 | 6.8 | 6.4 | 30.6 |

1) Boiling range of fraction, °C; 2) yield of fraction, % of fraction, 60°-200°; 3) unsaturated; 4) cyclic; 5) six-member; 6) five-member; 7) aromatic; 8) acyclic; 9) aromatic; 10) hexamethylene; 11) pentamethylene; 12) paraffinic.

the boiling point of the fraction rises when there is a corresponding reduction in the quantity of paraffinic hydrocarbons. Unsaturated hydrocarbons are completely absent or present in extremely insignifi-

cant quantities. Sulfur, nitrogen, and oxygen compounds are concentrated primarily in the gasoline tailings.

Thermal- and catalytic-cracking gasolines are more complex subjects for investigation than direct-distillation gasolines as a result of the fact that the former contain substantial quantities of unsaturated hydrocarbons capable of reaction.

The quantity of paraffinic and naphthenic hydrocarbons in thermal-cracking gasolines is determined primarily by the nature of the initial crude, and the content of unsaturated hydrocarbons is determined primarily by the refining regime. Here, as a rule, there are more aromatic hydrocarbons than in the direct-distillation gasolines produced from the same petroleums (Table 100).

An increase in the content of aromatic hydrocarbons in the thermal-cracking gasolines can be explained by the fact that the heavy fractions of petroleum, richer in aromatic hydrocarbons, serve as the crude for cracking; moreover, under the conditions of cracking the lower aromatic hydrocarbons are quite stable and are converted into gaseous products to a lesser extent than are the naphthenic and paraffinic hydrocarbons.

Among the paraffinic hydrocarbons in the thermal-cracking gasolines, pentane, hexane, heptane, octane, nonane, isohexane, trimethylethylmethane, diisopropyl, isopentane, isoheptane, etc. have been identified. The basic mass of the paraffinic hydrocarbons contained in thermal-cracking gasolines belongs to the normal or slightly branched paraffins.

The naphthenic hydrocarbons of thermal-cracking gasolines are derivatives of cyclopentane and cyclohexane. Among these, methylcyclopentane, cyclohexane, dimethylcyclopentane and methylcyclohexane, etc. have been identified. The presence of the tertiary carbon atom

has been established in naphthenic hydrocarbons.

Of the aromatic hydrocarbons, the greatest quantity of benzene has been found in the thermal-cracking gasolines, and here toluene, the xylenes, and the heavier alkylbenzenes predominate.

The unsaturated hydrocarbons of thermal-cracking gasolines are primarily monoolefins. The cycloolefins are contained in the middle and higher fractions of petroleum. 3- and 2-methylpentenes, 4- and 5-methylhexenes, hexene, some heptenes and octenes, methylcyclopentene, etc. have been identified.

The quantity of diolefinic hydrocarbons in thermal-cracking gasolines does not exceed 1%.

Piperylene and cyclopentadiene have been identified in the low-boiling fractions of gasoline through reactions with maleic anhydride.

The content of individual groups of hydrocarbons in various gasoline fractions produced by the thermal cracking of mazout from Groznyy paraffinic petroleum is presented in Table 101.

The catalytic-cracking gasolines are, in terms of chemical composition, unlike the thermal-cracking gasolines in that the former have a higher content of aromatic and isoparaffinic hydrocarbons. The content of unsaturated hydrocarbons in catalytic-cracking gasoline from a light crude (the kerosene-gas-oil fraction) is generally lower than in thermal-cracking gasolines. As the crude becomes heavier, the quantity of unsaturated hydrocarbons in the single-stage catalytic-cracking gasoline increases. Among the unsaturated hydrocarbons of the catalytic-cracking gasoline from a heavy crude, the olefins with straight and branched chains predominate. The quantity of these olefins amounts approximately to 50% of the over-all content of unsaturated hydrocarbons in the gasoline. Approximately 30% is made up of

unsaturated side chains linked with the aromatic nucleus. Diolefinic hydrocarbons with conjugate bonds may be present in substantial quantities in single-stage catalytic-cracking heavy-crude gasolines.

TABLE 102

Content of Hydrocarbon Groups (in %) in Catalytic-Cracking Gasoline [3]

| 1 Пределы выкипания фракции, °С | 2 Выход фракции, % от фракции 60—200 | 3 Непредельные | | | | 9 Ароматические | 10 Гексаметиленовые | 11 Пентаметиленовые | 12 Парафиновые |
|---|---|---|---|---|---|---|---|---|---|
| | | 4 циклические | | | 8 ациклические | | | | |
| | | 5 шестичленные | 6 пятичленные | 7 ароматические | | | | | |
| 60—95 | 30 | 0.4 | 6.5 | — | 9.1 | 5.1 | 4.7 | 18.3 | 55.9 |
| 95—122 | 17 | — | 7.0 | 2.5 | 3.3 | 16.5 | 16.8 | 15.0 | 39.9 |
| 122—150 | 18 | — | 5.3 | — | 6.3 | 42.6 | 12.7 | 7.7 | 25.4 |
| 150—200 | 35 | 2.0 | 1.2 | 0.7 | 3.1 | 60.3 | 6.8 | 4.4 | 21.5 |

1) Boiling range of fraction, °C; 2) yield of fraction, % of fraction, 60-200; 3) unsaturated; 4) cyclic; 5) six-member; 6) five-member; 7) aromatic; 8) acyclic; 9) aromatic; 10) hexamethylene; 11) pentamethylene; 12) paraffinic.

TABLE 103

Sulfur Content in Gasoline Distillates from Various Sources

| 1 Бензины | 2 Суммарное содержание серы, % | 3 Количество сернистых соединений, % | | | | | |
|---|---|---|---|---|---|---|---|
| | | 4 сероводород | 5 элементарная сера | 6 меркаптаны | 7 сульфиды | 8 дисульфиды | 9 остаточная сера*** |
| 10 Бензин прямой гонки из туймазинской нефти* | 0.096 | 10.4 | 3.4 | 22.1 | 36.0 | 9.5 | 18.6 |
| 11 Бензин термического крекинга из мазута туймазинской нефти** | 0.126 | 4.0 | 2.4 | 4.8 | 9.6 | 3.2 | 76.8 |
| 12 Бензин каталитического крекинга из фракции 350—450° туймазинской нефти | 0.185 | 0.0 | 4.9 | 3.8 | 14.1 | 3.4 | 71.8 |

1) Gasolines; 2) over-all content of sulfur, %; 3) quantity of sulfur compounds, %; 4) hydrogen sulfide; 5) elementary sulfur; 6) mercaptans; 7) sulfides; 8) disulfides; 9) residual sulfur***; 10) direct-distillation gasoline from Tuymazy petroleum*; 11) thermal-cracking gasoline from mazout of Tuymazy petroleum**; 12) catalytic-cracking [Key continued on following page]

[Key to Table 103 continued]: gasoline from 350-450° fraction of Tuymazy petroleum.

*According to data from A.S. Velikovskiy and S.N. Pavlova.
**According to data from A.V. Agafonov, B.G. Abayeva, and N.A. Okinshevich.
***Residual sulfur – conventional designation of remaining sulfur compounds in Faradzher analysis.

The distribution of the hydrocarbon groups in the fractions of the gasoline produced through the catalytic cracking of the kerosene-gas-oil fraction of the Groznyy paraffinic petroleum is presented in Table 102.

An examination of the data in Tables 101 and 102 will show a substantial difference between the content of unsaturated and aromatic hydrocarbons in thermal- and catalytic-cracking gasolines. The thermal-cracking gasoline contains 45% unsaturated hydrocarbons, and 11% aromatic hydrocarbons, whereas the catalytic-cracking gasoline, conversely, contains substantially more aromatic (33%) and less unsaturated (11%) hydrocarbons. The tendency to increase the concentration of aromatic hydrocarbons into higher-boiling fractions is particularly noticeable in the catalytic-cracking gasoline.

[illegible] in catalytic and thermal-cracking gasolines varies (see Tables 101 and 102); [illegible] six-member ring) in thermal-cracking gasoline, whereas this group of unsaturated hydrocarbons is virtually absent in the catalytic-cracking gasoline. The presence of unsaturated hydrocarbons with a five-member ring is greater by a factor of almost 3 in the thermal-cracking gasoline than in the catalytic-cracking gasoline.

The sulfur compounds are the most significant of the nonhydrocarbon admixtures in gasoline. Their presence substantially affects such operational properties of gasolines as their responsiveness to the



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tiknock agent, their tendency to oxidation and scale formation, their anticorrosion properties, etc. With an increase in the quantity of sulfur compounds in the gasoline, the operational properties of the gasoline are impaired.

In the direct-distillation gasolines produced from sulfur-bearing petroleums, the content of sulfur compounds is generally small. The basic mass of the sulfur compounds are found in the higher-boiling fractions of the petroleum. As these fractions are refined by means of thermal or catalytic cracking, the resultant gasolines contain more sulfur compounds than do the gasolines produced by the direct distillation of this same petroleum (Table 103).

The basic difference in the composition of the sulfur compounds in the gasolines obtained by the various refining processes from one and the same petroleum (Table 103) lies in the content of the so-called "residual sulfur." In the direct-distillation gasolines approximately 18.6% of the total sulfur content is contained in this residue, whereas in thermal- and catalytic-cracking gasoline "residual sulfur" amounts to 71.8 and 76.8%, respectively. The quantity of these compounds in the composition of the "residual sulfur" in the thermal- and catalytic-cracking gasolines is approximately identical, but there is a difference in quality, since it is substantially more difficult to purify the thermal-cracking gasolines of sulfur than is the case with the catalytic-cracking gasolines.

The oxygen compounds of gasolines pertain primarily to organic acids and phenols. These compounds are found basically in the high-boiling gasoline fractions. Cracking gasolines generally contain more oxygen compounds than direct-distillation gasolines.

Nitrogen compounds are contained in gasolines in insignificant quantities, and generally in the form of derivatives of pyridine and

similar nitrogen bases. In contradistinction to direct-distillation gasolines, in cracking gasolines we find only aromatic nitrogen bases.

## FRACTIONAL COMPOSITION OF AUTOMOTIVE GASOLINES

The fractional composition is the most important indicator of the quality of automotive gasolines, and on it depend the ease and reliability of starting, the warmup time, and responsiveness of the engine.

The general problems relating to vaporization and mixture formation in automotive engines were examined earlier (see Chapter 5); the problems associated with the effect of the fractional composition of gasolines on the behavior of engines under operating conditions are considered in this chapter.

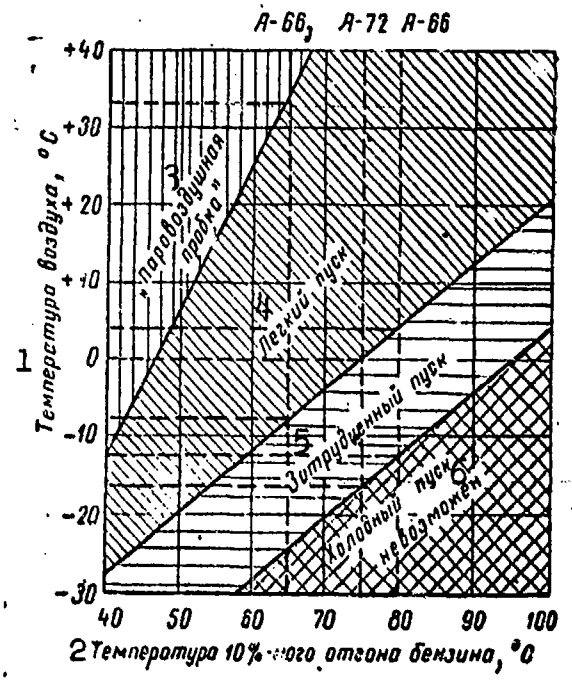


Fig. 140. Starting properties of automotive gasolines. 1) Air temperature, °C; 2) temperature of 10% distillation of gasoline, °C; 3) "vapor-air lock"; 4) easy start; 5) difficult start; 6) cold start impossible.

### The Starting of a Cold Engine

The easy starting of a cold engine depends in great measure on the quantity of easily vaporized fractions in the gasoline.

The possibility of starting a cold engine is generally associated with certain points on the standard gasoline-distillation curve (GOST 2177-48) and the pressure of its saturated vapors (GOST 1756-52).

Rather extensive projects have been carried out both in the USSR and abroad on evaluating the starting properties of gasolines, but no uniform requirements with

respect to the fractional composition of a gasoline to provide for engine start have as yet been worked out.

For example, N.V. Brusyantsev [11] maintains that in order to provide for the starting of automotive engines during the winter in the central belt of the Soviet Union at an air temperature of -20° or higher it is necessary for the 10% distillation temperature of the gasoline being used to be no higher than 76-78° (under the condition that use is made of corresponding grades of lubrication oils which will provide for rather easy turning of the crankshaft of the engine at this temperature).

In the proposals of the NAMI [State All-Union "Order of Labor Red Banner" Automobile and Automobile Engine Scientific Research Institute] with respect to the new specifications for domestic automotive gasolines [12] provision has been made for a reduction of the 10%-distilled temperature to 60° (in the place of the 75-79° according to the GOST 2084-56) for summer gasoline grades and to 50° in the place of 65° for winter grades.

According to the data of A.S. Irisov [17] (Fig. 140) the A-72 gasoline, having a 10%-distilled temperature below 70°, must provide for the start of a cold engine to a temperature of -17° or above, and the winter A-66 gasoline (10% boils over below 65°) must provide for the start of a cold engine at a temperature of -24° or above.

In Great Britain, where the air temperature during the winter rarely falls below -7°, it is felt that in order to provide for the satisfactory starting of a cold engine it is necessary for 10% of the winter gasoline grade to be distilled below 60°. For the summer gasoline grade the distillation temperature (10%) may be raised to 70° [13].

In the USA, in recent years, the ease and reliability of starting

a cold engine has been associated with the quantity of light fractions in the gasoline, said fractions boiling over below 70° [14, 15]. It is felt that the starting of an engine at an air temperature of -20° meets with no difficulty if the gasoline being used contains more than 20% of light fractions boiling over below 70° (Fig. 141).

TABLE 104

Properties of Automotive Gasolines Tested for Engine Start

| 1 Показатели | 2 № образцов | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 3 Фракционный состав (перегоняется при температуре, °С): | | | | | | | |
| 4 н. к. | 34 | 41 | 43 | 46 | 55 | 56 | 63 |
| 10% | 48 | 59 | 64 | 68 | 75 | 77 | 86 |
| 20% | 55 | 68 | 73 | 78 | 84 | 85 | 92 |
| 30% | 63 | 76 | 80 | 85 | 92 | 93 | 99 |
| 40% | 71 | 88 | 89 | 93 | 100 | 100 | 107 |
| 50% | 81 | 95 | 101 | 103 | 110 | 108 | 113 |
| 60% | 94 | 109 | 113 | 113 | 120 | 118 | 124 |
| 70% | 109 | 126 | 127 | 127 | 134 | 134 | 138 |
| 80% | 129 | 143 | 143 | 143 | 147 | 145 | 151 |
| 90% | 157 | 168 | 168 | 166 | 166 | 166 | 167 |
| 5 к. к. | 187 | 187 | 187 | 187 | 187 | 187 | 189 |
| 6 Испаряемость до 70°С, % | 38 | 24 | 16 | 12 | 6 | 5 | 1 |
| 7 Давление насыщенных паров (ГОСТ 1756-52), мм рт. ст. | 547 | 430 | 310 | 230 | 203 | 194 | 189 |
| 8 Предельные температуры воздуха, при которых возможен пуск холодного двигателя, °С | −26 ÷ −27 | −21 ÷ −22 | −18 ÷ −19 | −16 ÷ −17 | −12 ÷ −13 | −11 ÷ −12 | −7 ÷ −8 |

1) Indicator; 2) specimen No.; 3) fraction composition (distilled at a temperature, °C); 4) start of boiling; 5) end of boiling; 6) vaporizability below 70°C, %; 7) pressure of saturated vapors (GOST 1756-52), mm Hg; 8) limit air temperatures at which cold-engine start is possible, °C.

In order to refine the requirements imposed on the fractional composition of gasolines and to clarify the starting properties of these gasolines, tests on seven gasoline specimens [35] were carried out, each gasoline differing from the other in terms of the content of light fractions. These specimens were prepared on a base of the commercial automotive gasoline A-72 by distillation or through the

TABLE 105

Data of Various Investigations Into the Effect of the 10%-Distilled Temperature of a Gasoline on the Starting Properties of this Gasoline

| 1 Температура перегонки 10% бензина, °С | 2 Минимальная температура воздуха, при которой возможен пуск двигателя, °С | | |
|---|---|---|---|
| | 3 по данным Брауна [см. 10] | 4 по данным Ковдерая и Виттерса [19] | 5 по данным испытаний двигателя ГАЗ-51 |
| 48 | —22 | —26 | —26÷27 |
| 59 | —12 | —19 | —22÷23 |
| 64 | —8 | —15 | —18÷19 |
| 68 | —5 | —13 | —16÷17 |
| 75 | —1 | —8 | —12÷13 |
| 77 | +3 | —7 | —11÷12 |
| 86 | +10 | —1 | —7÷8 |

1) Distillation temperature (10%) of gasoline, °C; 2) minimum air temperature at which engine start is possible, °C; 3) data after Braun [see 10]; 4) data after Cowderay and Witters [19]; 5) data from tests of GAZ-51 engine.

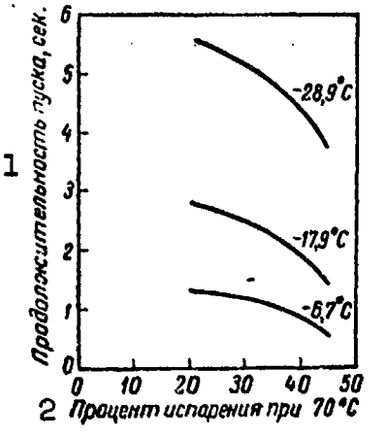


Fig. 141. Effect of vaporizability and air temperature on duration of start. 1) Duration of start, sec; 2) percent of vaporization at 70°C.

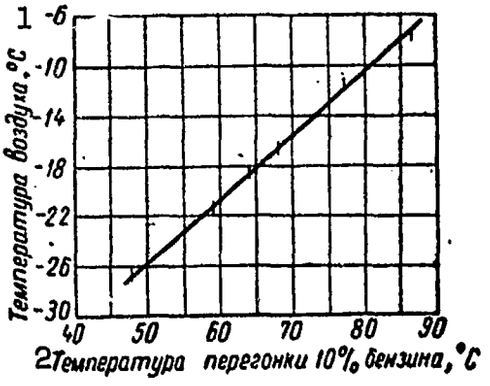


Fig. 142. Limit air temperature at which cold-engine start is possible as a function of the 10%-distilled temperature of the gasoline. 1) Air temperature, °C; 2) 10%-distilled temperature of the gasoline, °C.

dition of light fractions (Table 104).

The tests were carried out during the winter in an automobile-laboratory equipped with a GAZ-51 engine, with the temperature of the surrounding air at -27° or higher. For the crankcase oil a low-viscosity motor oil was used, since this oil made it possible to obtain

the number of engine revolutions required to start the engine at an air temperature of -27° or higher.

Figures 142, 143, and 144 show the limit air temperatures at which engine start is possible as a function of the fractional composition and the pressure of the saturated vapors of the gasolines being investigated.

The limit starting temperatures for engines operating on gasolines of various fractional compositions is virtually directly proportional to the value of the 10%-distilled temperatures of the gasoline (Fig. 142).

The data that were obtained on the effect that the 10%-distilled temperature of the gasoline has on the starting properties of the gasoline and the earlier-published results of the investigations are presented in Table 105.

The limit starting temperatures that have been determined are substantially lower than those presented by Braun [10], and somewhat lower than those determined by Cowderay and Witters [19]. The divergence in the data can be explained by the differences in the designs of the test engines, the properties of the lubricants employed, and the methods by which the tests were carried out.

On the basis of the obtained results, the following formula may be recommended for practical utilization:

$$t_v = t_{10\%}/2 - 50.5,$$

where $t_v$ is the minimum air temperature at which engine start is possible, in °C; $t_{10\%}$ is the 10%-distilled temperature of the gasoline, in °C.

The tests that were carried out showed that in order to start a cold engine during the winter, under the climatic conditions of the

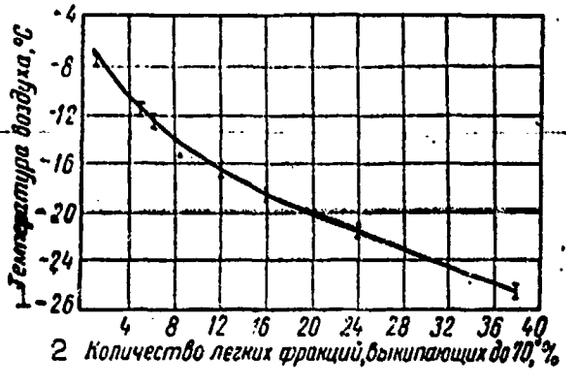


Fig. 143. Limit air temperature at which cold-engine starts are possible as a function of the quantity of light fractions boiling over below 70°. 1) Air temperature, °C; 2) quantity of light fractions boiling over below 70°, %.

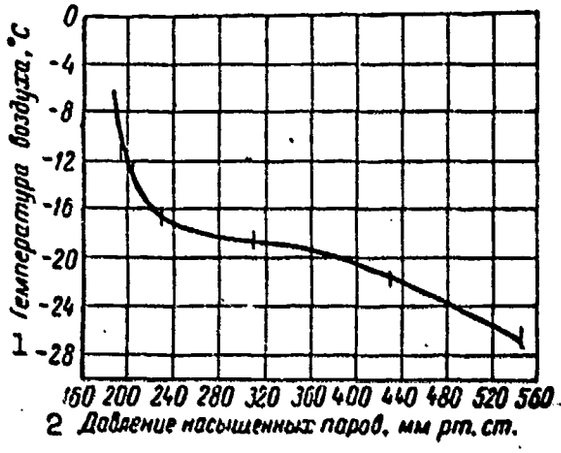


Fig. 144. Limit air temperature at which cold-engine starts are possible as a function of the pressure of the saturated gasoline vapors (GOST 1756-52). 1) Air temperature, °C; 2) pressure of saturated vapors, mm Hg.

northern and central belts of the Soviet Union (at an air temperature ranging between -20 and 25°) the 10%-distilled temperature of the gasoline should not exceed 50-60°, and no less than 20-25% of the gasoline should boil over below 70° (see Fig. 143).

The relationship between the minimum air temperature for engine start and the pressure of the saturated vapors of the gasolines employed is quite characteristic (see Fig. 144). With a reduction in the pressure of the saturated gasoline vapors to 250-260 mm Hg, the starting properties of the gasoline are impaired virtually rectilinearly. The reduction of the pressure of the saturated vapors below 250 mm Hg is accompanied by a pronounced impairment of the starting properties. These data indicate the need for limiting the lower limit of the pressure of the saturated vapors of automotive gasolines. To provide for engine starting even in relatively warm weather, the pressure of the saturated gasoline vapors should not be below 250 mm Hg.

The upper limits of the pressure for the saturated vapors of domestic automotive gasolines (700 mm Hg for the winter grades of gaso-

TABLE 106

Effect of Air Temperature on Gasoline Consumption and Duration of Cold-Engine Start of "Moskvich" Automobile [20]

| 1 Температура воздуха, °С | 2 Продолжительность пуска (в сек.) на бензине, 10% которого испаряется при | | 3 Расход топлива (в мл) при пуске на бензине, 10% которого испаряется при | |
|---|---|---|---|---|
| | 79° | 72° | 79° | 72° |
| 0 | 10,5 | 9,4 | 10,0 | 8,7 |
| −8 | 45,0 | 29,0 | 48,0 | 30,0 |
| −16 | 515,0 | 225,0 | 678,0 | 399,0 |

1) Air temperature, °C; 2) duration of start (in seconds) with gasoline of which 10% vaporizes at; 3) fuel consumption (in ml) during starts with gasoline of which 10% vaporizes at.

line and 500 mm Hg for all of the remaining grades) satisfy the requirements of automotive engines in terms of the starting properties of gasolines.

The starting of a cold engine depends not only on the fractional composition of the gasoline being used, but on the quality of the lubricant as well, and on the design of the carburetor, the intake manifold, and a number of other factors. However, the starting of each engine is doubtlessly facilitated by the utilization of gasolines which contain a greater number of the light fractions which boil over below 70°, which exhibit a lower 10%-distilled temperature, and a higher pressure of saturated vapors.

It should be borne in mind that an increase in the time required to start an engine functioning on a gasoline which exhibits poor vaporization properties will, naturally, be accompanied by an increase in the fuel consumption (Table 106).

As the temperature of the surrounding air drops, the quantity of gasoline consumed in the starting of the engine increases; the consumption of a gasoline which exhibits poor vaporization properties increases particularly sharply (see Table 106).

It is possible to improve the starting characteristics of gasolines by lightening their fractional composition only within certain limits. The utilization of extremely light gasolines in an engine results in other operational difficulties – the formation of vapor locks in the fuel manifolds and the gushing of the fuel through the carburetor jets.

Formation of vapor locks

In automobile operation it has been noted that the light gasolines which are capable of vaporizing intensely at the temperature being evolved beneath the hood of a heated and normally functioning en-

| 1 Температура отгона 10% бензина, °С | 2 Температура начала образования паровых пробок, °С |
|---|---|
| 40 | —13 |
| 50 | +7 |
| 60 | +27 |
| 70 | +47 |
| 80 | +67 |

1) 10%-distilled temperature of gasoline, °C; 2) temperature of beginning of formation of vapor locks, °C.

gine can form so-called "vapor locks" in the fuel manifolds and the carburetor channels. The fuel begins to enter through the carburetor jet in the form of a foam consisting of liquid gasoline and carrying (in suspension) numerous air and gasoline-vapor bubbles. Here the quantity of gasoline (by weight) employed for the preparation of the mixture diminishes sharply and the combustible mixture is drastically leaned; the engine begins to "sputter" and may stall [18].

The formation of vapor locks is much more serious in the summer than it is in the winter, and particularly in those regions situated high above sea level. Therefore, many countries have developed special grades of gasoline for use within a specific climatic zone and for a

definite time of the year. During the winter gasolines with a greater quantity of easily vaporizing fractions are used to provide for ease of engine start in cold weather, whereas during the summer gasolines are used with a lower tendency to vaporize, this in order to prevent the formation of the vapor locks.

The most favorable conditions for the formation of vapor locks are present as an engine is stopped in hot weather. In this case, the engine compartment is no longer ventilated, and the air temperature rises sharply; the gasoline in the fuel manifold then heats up drastically. These conditions favor intensive gasoline vaporization and the formation of vapor locks, as a result of which it is impossible to start the engine even if the automobile has been brought to a stop for only a short period of time.

As the engine is stopped, and sometimes during engine operation, we can observe yet another phenomenon that is associated with the excessive vaporization of the gasoline in the engine fuel-feed system — this is the gushing of the fuel through the carburetor jets. The gasoline vapors may collect in the bottom part of the carburetor flow chamber, thus forcing the liquid gasoline into the intake system of the engine. The ejected gasoline forms a somewhat overly rich mixture and the normal operation of the carburetor is disrupted. This phenomenon has been designated as "percolation."

The air temperature ($t_v$) at which the formation of vapor locks is possible is associated with the 10%-distilled temperature ($t_{10\%}$) of the gasoline by the following equation [10]:

$$t_v = 2t_{10\%} - 93.$$

In calculations with this formula, we obtain values of the temperatures for the beginning of the formation of vapor locks as func-

tions of the vaporizability of the gasoline being employed.

In accordance with these data and the results presented earlier on the effect that the 10%-vaporization temperature of the gasoline has on the start of an engine (see Fig. 142), a gasoline with a 10% point equal to 50° may be used successfully at an air temperature ranging from -26° (from the starting of the cold engine) to +7° (to the formation of vapor locks); a gasoline with a 10% point equal to 60° may be used at an air temperature ranging from -20° to +27°; a gasoline with a 10% point equal to 70° may be used in an air temperature range from -15° to +47°, and a gasoline with a 10% point equal to 80° may be used within a temperature range of -10° to +67°.

The temperatures presented above can be used only as tentative data for a determination of the adaptability of a given gasoline specimen, since the pressure of the saturated gasoline vapors and the structural features of the engine's fuel system have not been taken into consideration here.

To calculate the temperature for the beginning of the formation of vapor locks, we propose the following formula which associates this indicator exclusively with the magnitude of the saturated-vapor pressure, after Reyd [sic] [10]:

$$t_v = 260 - 77.8 \log P_r,$$

where $t_v$ is the temperature of the beginning of the formation of vapor locks, in °C; $P_r$ is the pressure of the saturated gasoline vapors, according to Reyd [sic], in mm Hg.

Calculations in accordance with this formula show that a gasoline exhibiting a saturated-vapor pressure of 500 mm Hg will form vapor locks at a temperature above +50°, whereas a gasoline with a saturated-vapor pressure of 700 mm Hg will form vapor locks at +39°.

These data pertain to the operation of automobiles in lowland regions, at sea level. With greater altitude, vapor locks may form at lower temperatures.

Industrial specifications for domestic automotive gasolines permit a saturated-vapor pressure of up to 500 mm Hg for summer grades and up to 700 mm Hg for winter grades. In the proposals of the NAMI [12] on the new specifications for automotive gasolines provision is made for the reduction of the permissible level of saturated-vapor pressure to 450 and 600 mm Hg, respectively.

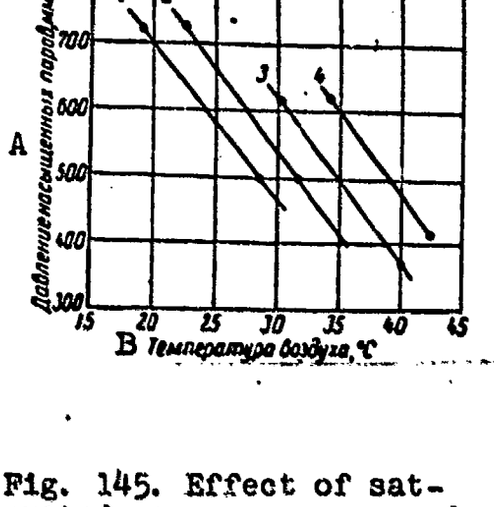


Fig. 145. Effect of saturated-vapor pressure and gasoline vaporizability on the formation of vapor locks at various temperatures. Up to 70° the following gasolines vaporize, %: 1) 40; 2) 30; 3) 20; 4) 10. A) Saturated-vapor pressure, mm Hg; B) air temperature, °C.

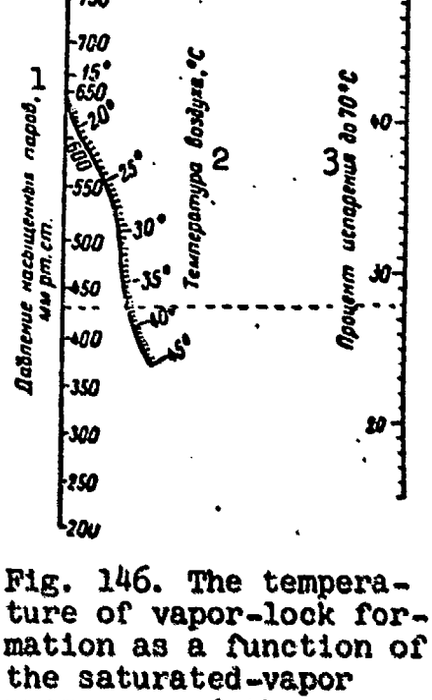


Fig. 146. The temperature of vapor-lock formation as a function of the saturated-vapor pressure and the vaporizability of the gasoline (nomogram). 1) Saturated-vapor pressure, mm Hg; 2) air temperature, °C; 3) percentage vaporized below 70°C.

A more exact idea as to the temperatures prevailing for the initiation of vapor-lock formation in the engine feed system can be obtained by studying the effect of two indicators simultaneously, i.e., we have reference here to the pressures of the saturated gasoline va-

pors and the quantity of light fractions in the gasoline.

Figure 145 shows the temperature of the beginning of vapor-lock formation as a function of the pressure of the saturated gasoline vapors and the percentage of gasoline vaporizability below 70° [16]. A gasoline exhibiting a saturated-vapor pressure of 500 mm Hg will form vapor locks at an air temperature ranging from 29 to 39° depending on the content of light fractions (boiling over below 70°) within the gasoline.

For the practical determination of the temperature at which the formation of vapor locks in engines begins with the utilization of a given gasoline, we recommend the nomogram [15] obtained through the evaluation of the test results carried out on many automobiles of various makes (Fig. 146). As a result of the investigations it was determined that this indicator is far from constant.

The variations in the designs of the fuel-feed systems are responsible for the divergence in the obtained results. The temperature attained by the gasoline in the system is a function of the layout of the manifolds, the functioning of the thermostats and the radiator louvers, the ventilation of the engine compartment, and similar automobile features. The cited relationships between the vaporizability of the gasolines and their tendency toward vapor-lock formation can be used only for a tentative evaluation of the suitability of a given gasoline for utilization under the given temperature conditions.

Warmup and Responsiveness of Engine

The time required for the warmup of an engine depends in great measure on the fractional composition and the nature of the distillation curve for the gasoline being used. The quantity of light and medium fractions in the gasoline, as well as the 90%-vaporization temperature of the gasoline affect the warmup of the engine. In addi-

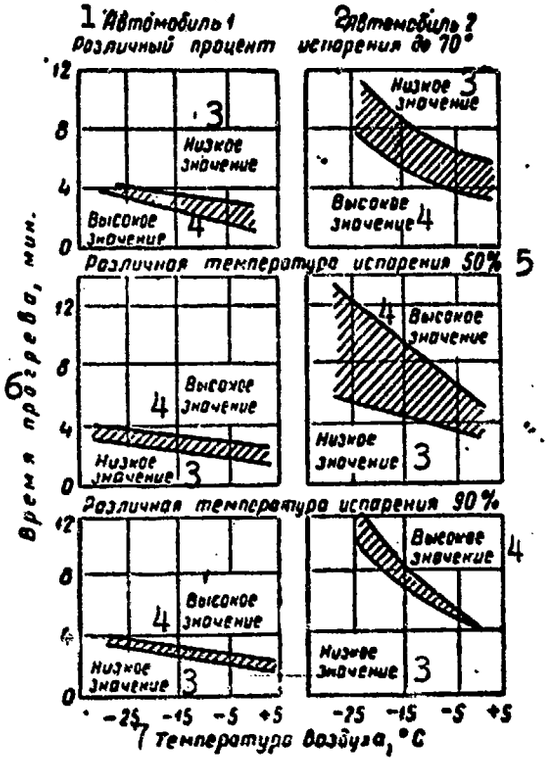


Fig. 147. Effect of automobile design on warmup duration. 1-2) Automobile 1 – automobile 2, varying percentage of vaporization below 70°; 3) low value; 4) high value; 5) varying 50% vaporization temperature; 6) warmup time, minutes; 7) air temperature, °C.

tion to the fractional composition of the gasoline, the structural features of the engine also have a substantial effect on the time required for engine warmup. The relative effect of a change in the curve of the fractional gasoline distillation on the warmup time of two types of engines is shown in Fig. 147 [14].

The engine of the first automobile proved to be only slightly sensitive to changes in the fractional composition of the fuel [14], whereas the warmup time of the engine in the second automobile changed significantly as gasolines having various quantities of light and medium fractions were used (see Fig. 147).

The 50%-vaporization temperature of the gasoline has the most significant effect on the warmup time of the engine. The higher this temperature, the longer the period of time required to warm up the engine.

In the proposals of the NAMI [12] on the new specifications for domestic gasolines, it is suggested that the 50%-vaporization temperature of gasoline be lowered to 115° for the summer grades, and to 105° for winter grades.

To determine the duration of engine warmup on a given gasoline,

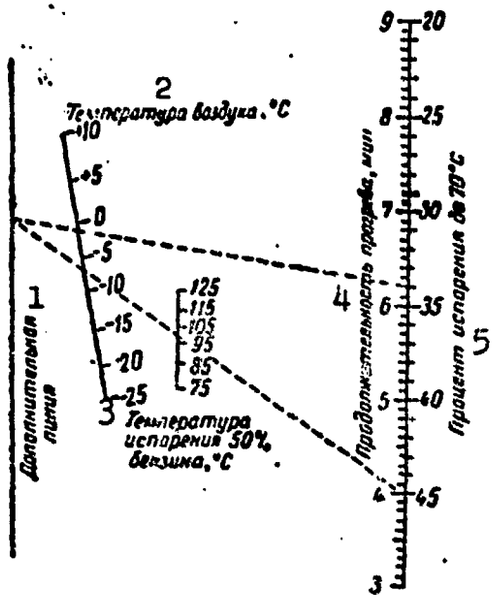


Fig. 148. Duration of engine warmup as a function of gasoline vaporizability and the air temperature (nomogram). 1) Additional line; 2) air temperature, °C; 3) 50% vaporization temperature of gasoline, °C; 4) duration of warmup, minutes; 5) percentage of vaporization below 70°C.

we can use the nomogram (Fig. 148) compiled from an evaluation of the test results from six automobiles of various designs.

By the term "responsiveness" of an engine we mean the speed with which the rpm of a completely heated engine can be increased as the throttle is opened abruptly. The responsiveness of an engine is a function of the fractional composition of the gasoline (primarily of the 50%-vaporization temperature of the gasoline) and the design of the engine's intake system.

The automobile will accelerate satisfactorily if the gasoline pro-

TABLE 107

Effect of Fractional Composition on Responsiveness of GAZ-51 engine without load*

| 1 Время с момента открытия дроссельной заслонки, сек. | 2 Суммарное число оборотов двигателя после открытия дроссельной заслонки на бензине следующего фракционного состава | | | | |
|---|---|---|---|---|---|
| | 50% испаряется до 3 97°; к. к. 171° | 50% испаряется до 4 107°; к. к. 175° | 50% испаряется до 5 112°; к. к. 180° | 50% испаряется до 6 120°; к. к. 182° | 50% испаряется до 7 128°; к. к. 185° |
| 1/8 | 9.0 | 9.0 | 8.0 | 7.0 | 7.0 |
| 2/8 | 23.5 | 23.0 | 20.5 | 18.5 | 19.5 |
| 3/8 | 44.0 | 41.0 | 40.0 | 38.0 | 38.5 |
| 4/8 | 70.0 | 68.0 | 66.0 | 60.5 | 59.5 |
| 5/8 | 100.0 | 100.0 | 95.5 | 88.5 | 88.5 |
| 6/8 | 136.0 | 132.0 | 131.0 | 132.5 | 130.0 |
| 7/8 | 176.5 | 172.0 | 165.5 | 162.0 | 159.5 |
| 1 | 221.0 | 216.0 | 211.5 | 203.5 | 200.0 |

* After the data of A.A. Gureyev, M.A. Senichkin, and P.G. Filatov. [Key on following page]

[Key to Table 107]: 1) Time from instant of throttle opening, sec; 2) total engine rpm after opening of throttle, when operating on a gasoline of the following fractional composition; 3) 50% vaporizes below 97°; end of boiling, 171°; 4) 50% vaporizes below 107°; end of boiling, 175°; 5) 50% vaporizes below 112°; end of boiling, 180°; 6) 50% vaporizes below 120°; end of boiling, 182°; 7) 50% vaporizes below 128°; end of boiling, 186°.

vides for a fuel-air-mixture composition equal to 1:12 (by weight). If the gasoline exhibits less satisfactory vaporizability, leaner mixtures are formed – having compositions of 1:16, 1:18, and 1:20 – and the time required for acceleration increases by 9.37 and 170%, respectively [22].

We have carried out experiments to study the effect that the fractional composition of a gasoline has on the responsiveness of the GAZ-51 engine, without load (Table 107).

We can see from the data in Table 107 that the quantity of medium and tailing fractions in the gasoline has a substantial effect on the responsiveness of the engine. In tests carried out with the engine under load the difference between the gasolines, in terms of the speed with which the rpm can be increased, may prove to be even more significant.

The Effect of the Fractional Composition of Gasolines on Engine Wear

The completeness of gasoline vaporization in an engine is characterized by the 90%-distilled temperatures of the gasoline and the end of gasoline boiling. With high values for these temperatures, the heavy gasoline fractions do not vaporize in the intake manifold of the engine and enter the cylinders in liquid form. The liquid portion of the gasoline vaporizes in the combustion chamber, but not completely, and the unvaporized portion flows through the seals of the piston rings into the crankcase of the engine. In this case, the lubricant is flushed away from the walls of the cylinders and the oil in the crankcase is diluted. At those points where the lubricant is

flushed away semidry friction of component parts takes place and this is accompanied by an increase in wear.

Particularly intensive engine wear takes place if the engine is started while cold and gasolines of a heavy fractional composition are used. In this case the liquid form of the gasoline enters, in large quantities, the engine cylinders and there is serious flushing of the lubricant from the walls. It was pointed out earlier that with a drop in the air temperature and an impairment in the fractional composition of the gasoline the time required to start the engine increases as does the quantity of fuel expended on the start (see Table 106).

N.V. Brusyantsev [23] found that it is primarily those gasoline fractions that boil over above 180° that enter the crankcase oil. Here there is a certain reduction in the viscosity of the lubricating oil. However, the basic factor responsible for increased wear of automotive engines with the utilization of fuels exhibiting poor vaporizability is not the dilution of the crankcase oil, but the flushing of the lubricant from the rubbing surfaces of the component parts by the unvaporized fuel. The degree of oil dilution in the crankcase can be considered as an indicator only of the fact that the lubricant is being flushed away in the engine and that this produces increased wear.

The relationship between the temperature of the end of gasoline boiling and the over-all engine wear during operation with these gasolines is presented in Fig. 149.

In addition to increased wear, fuel consumption (Fig. 150) increases with the utilization of gasolines exhibiting a high end-of-boiling temperature, and there is an intensification of the distribution nonuniformity in the composition (in %) of the combustible

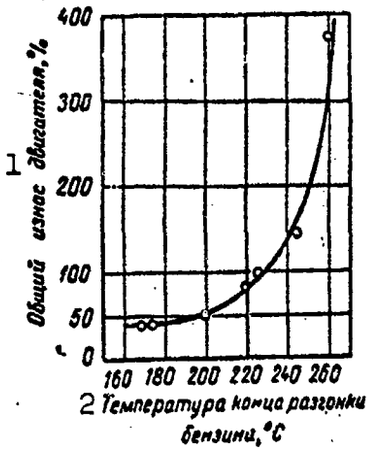


Fig. 149. The effect of the end of gasoline distillation on engine wear. 1) Total engine wear, %; 2) temperature of end of gasoline distillation, °C.

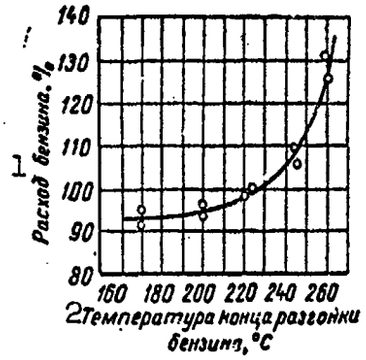


Fig. 150. Effect of end of gasoline distillation on gasoline consumption during automobile operation. 1) Gasoline consumption, %; 2) temperature of end of gasoline distillation, °C.

mixture through the cylinders of the engine [24].

90% gasoline vaporizes at the following temperature, °C:

| | |
|---|---|
| 115 | 3.0 |
| 120 | 3.2 |
| 130 | 4.4 |
| 140 | 8.0 |
| 150 | 14.6 |
| 154 | 18.0 |

End of gasoline boiling, °C:

| | |
|---|---|
| 135 | 3.0 |
| 140 | 3.1 |
| 150 | 3.2 |
| 160 | 3.4 |
| 170 | 4.8 |
| 177 | 18.0 |

Domestic automotive gasolines exhibit an end-of-boiling temperature of 205° (A-66 gasoline) and 195° (A-72 gasoline), and the 90%-distilled temperature is, respectively, equal to 195° and 180°. The winter gasoline for the regions in the North and in Siberia exhibit an end-of-boiling temperature of 190° and a 90%-distilled temperature

of 175°.

With a reduction in the end-of-boiling point for automotive gasolines, the operational properties of the gasolines show substantial improvement, but the available quantity is reduced.

Carburetor Icing

The vaporization of gasoline in the intake system of an engine is accompanied by a drop in the temperature of the fuel-air mixture as a result of the fact that the heat required for vaporization (the heat of vaporization) is taken primarily from the air in which the vaporization takes place, and from the metallic component parts of the intake system. It has been noted, for example, that at an ambient-air temperature of +7.5°, the temperature of the throttle drops to −14° within 2 minutes.

As a result of the reduction of the temperature in the fuel-air mixture, the moisture in the air freezes and condenses on the cold component parts of the intake system, forming an ice crust. As the throttle ices up, the flowthrough section of the carburetor is reduced. At low rpm, and incomplete engine load, the quantity of the injected fuel-air mixture is reduced, the engine rpm is lowered, the operation of the engine becomes intermittent, and this latter is accompanied by the shaking of the entire engine. Under particularly unfavorable conditions, the throttle may freeze to the diffuser and the engine will stop.

As a result of the formation of ice on the jets, the flow of gasoline is interrupted, the combustible mixture is leaned, and the engine rpm is reduced.

The degree of carburetor icing is a function of both the temperature and humidity of the air, as well as of the design of the intake system, the vaporizability of the gasoline, and the latent heat of

vaporization of the components of the gasoline.

Carburetor icing is particularly pronounced on cold raw days, or under conditions of rain or fog (Fig. 151). The greatest stoppage of engine operation as a result of carburetor icing is observed at 100% relative humidity and at an ambient-air temperature of about 4.5° [16]. A temperature of 11° is somewhat too high for carburetor icing, whereas at a temperature below 1.7°, even in saturated air, there is too little water in order to cause carburetor icing.

In the case of easily vaporizing fuels, the almost complete vaporization of these fuels ceases in the carburetor, which is the reason why the carburetor cools off more drastically and carburetor icing occurs more frequently [25] and within a wider range of temperatures and relative air humidity.

Investigations have shown [13] that in all cases in which the vaporization temperature of 10%-, 50%-, and 90%-distilled gasoline is increased, carburetor icing diminishes. The greatest effect is produced by increasing the 10%-distilled temperature of a gasoline, while the least influence is exerted by the vaporization temperature of a 90% gasoline.

The prevention of carburetor icing by means of raising the vaporization temperature of 10% gasoline has not gained widespread acceptance, since the starting properties of the gasoline are impaired in this case.

Carburetor icing can be effectively countered by heating the combustible mixture or the air in the intake manifold of the engine. The mixture must be heated so that the temperature of the mixture does not drop below +3° with total fuel vaporization, i.e., below that temperature at which there is as yet no freezing of the moisture being condensed in the intake system of the engine, regardless of the

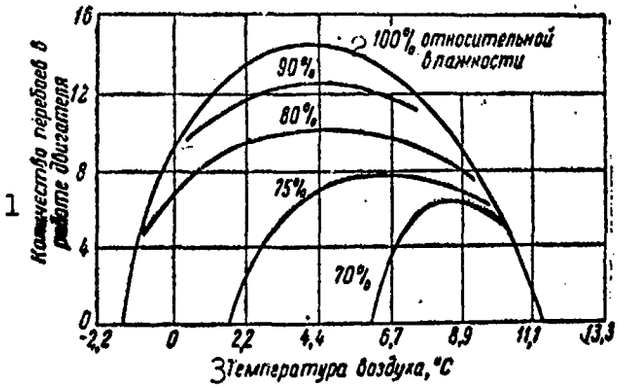


Fig. 151. Carburetor icing as a function of air temperature and humidity. 1) Number of stoppages in engine operation; 2) 100% relative humidity; 3) air temperature, °C.

air humidity.

If the intake manifold is heated, the fill factor for the combustion chamber is reduced as is engine power; therefore this means of combating carburetor icing can be employed only in certain limited cases.

In recent times, special antiicing gasoline additives have gained widespread acceptance in the effort to control carburetor icing [27] (see Chapter 14).

In an examination of engine requirements with respect to fractional composition of gasolines it has been demonstrated that the best operating conditions are provided in each climatic zone, depending on the time of year, by using gasolines exhibiting optimum fractional composition. During the winter the light gasolines are most effective, whereas for summer operation heavier gasolines can be used. The suitability of gasolines of various fractional composition for particular engines depends in great measure on the structural features of the intake system of the engine.

ANTIKNOCK PROPERTIES OF AUTOMOTIVE GASOLINES

The development of the automobile manufacturing industry is accompanied by an improvement in the operational characteristics of engines.

Increasing the compression ratio is one of the basic and most important trends in the development of automotive engines. Through an

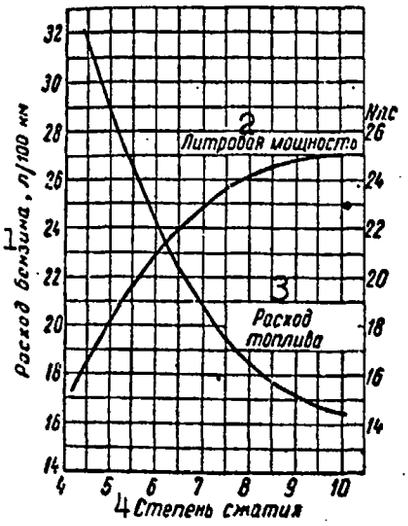


Fig. 152. Effect of compression ratio on fuel consumption and the per-liter horsepower of the engine. 1) Fuel consumption, 1/100 km; 2) per-liter horsepower; 3) fuel consumption; 4) compression ratio.

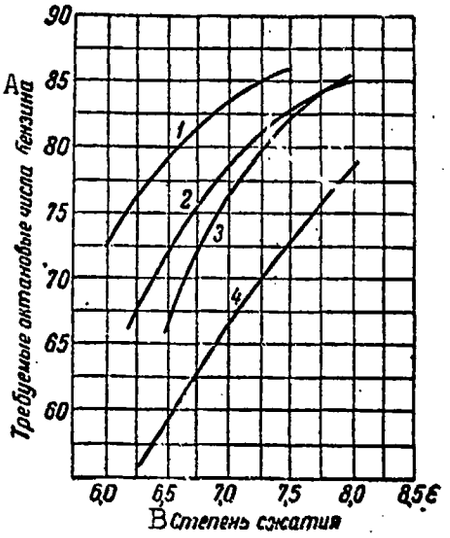


Fig. 153. Effect of compression ratio in engine on octane numbers of automotive gasolines. Engines: 1) ZIS-120; 2) GAZ-51; 3) GAZ-M20; 4) MZMA-401; A) required gasoline octane numbers; B) compression ratio.

increase in the compression ratio there is a simultaneous improvement in two other basic indicators as well – the per-liter horsepower output of the engine is increased and the gasoline consumption is reduced (Fig. 152). These indicators can be improved only if a gasoline exhibiting the appropriate antiknock values is used. With increased compression ratios for engines, the requirements with respect to antiknock stability of gasolines increases (Fig. 153). Consequently, each automotive engine requires a gasoline with definite antiknock

properties, depending on the compression ratio and other structural factors.

When using gasolines whose antiknock stability does not satisfy engine requirements it becomes necessary to reduce the crank-angle lag. The reduction of the crank-angle lag below its optimum value reduces engine power and impairs engine economy. As an illustration let us examine the road knock rating of the "Moskvich-407" engine.

Figure 154 shows [28] the change in the dynamics of automobile acceleration (in direct drive, the time required to accelerate from 30 to 70 km/hr), the change in fuel economy (the consumption of fuel per 100 km at a constant speed of 30 and 70 km/hr and in accelerating the automobile from 30 to 70 km/hr) and the required octane numbers of the gasoline (the angles of the initial ignition setting, causing knock in operations with reference mixtures having various octane numbers).

The antiknock properties of automotive gasolines are the most important operational indices of gasoline quality. The expansion of the automobile-making industry is accompanied by a constant rise in engine requirements with respect to the antiknock stability of the fuels being used.

One of the most important tasks of the Seven-Year Plan (1959-1965) is the achievement of improved qualities of petroleum products, including automotive gasolines.

The relationship between the production of automotive gasolines exhibiting various values for antiknock stability in recent years and in the Seven-Year Plan is presented in Table 108.

Automotive gasolines are a complex mixture of hydrocarbons of various structures and, therefore, the antiknock stability of individual hydrocarbon fractions may differ from the antiknock stability

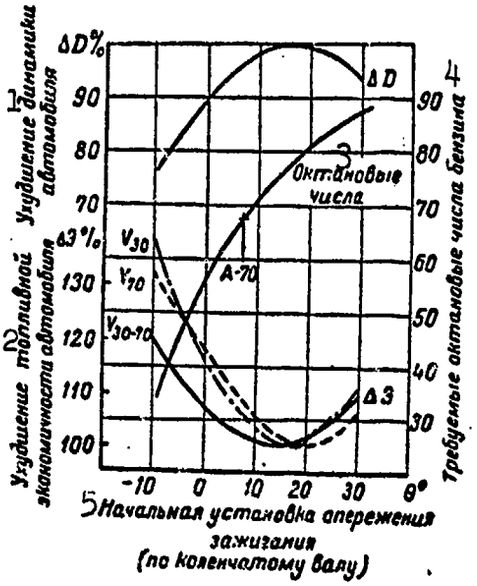


Fig. 154. Road knock rating of "Moskvich-407" automobile. 1) Impairment of automobile dynamics; 2) impairment of fuel economy of automobile; 3) octane numbers; 4) required gasoline octane numbers; 5) initial crank-angle lag setting.

of a gasoline as a whole. Table 109 shows data on the antiknock properties of 25% fractions of direct-distillation [B-70] and thermal-cracking [A-70] gasolines.

The head fractions of gasolines exhibit the highest octane numbers, and as the boiling point of the fractions of these gasolines rises, the antiknock stability of the gasolines is reduced. In this connection, the lightening of the fractional composition of direct-distillation and thermal-cracking gasolines will result in an increase in the octane numbers of these gasolines as a result of a drop in the end-of-boiling temperature.

TABLE 108

Production Figures for Automotive Gasolines in the USSR (in %) [2, 21]

| 1 Марка бензина | 1955 г. | 1956 г. | 1958 г. | 1959 г. | 1960 г. | 1965 г. |
|---|---|---|---|---|---|---|
| А-66 | 47,5 | 66,8 | 73,0 | 75,2 | 95,0 | 58,6 |
| 2 А-70*, А-72 и выше | 7,0 | 3,7 | | 4,7 | | 4 Более 40 |
| 3 Бензины с октановым числом менее 66 | 45,5 | 29,5 | 27,0 | 20,1 | 5,0 | — |

* The production of A-70 gasoline was suspended in 1962.

1) Gasoline brand; 2) A-70*, A-72, and higher; 3) gasolines with octane numbers below 66; 4) over 40.

For example, the thermal-cracking Moscow Petroleum Refinery gas-

TABLE 109

Antiknock Values of 25% Fractions of A-70 and B-70 Gasolines

| 1 Бензины | 2 Пределы выкипания фракций, °С | 3 Количество фракций, % | 4 Плотность, г/см³ | 5 Октановое число | |
|---|---|---|---|---|---|
| | | | | 6 моторный метод | 7 исследовательский метод |
| А-70 | 8 Исходный | 100 | 0,7439 | 69,3 | 75,0 |
| | 9 н. к. —90 | 25 | 0,6984 | 74,7 | 83,4 |
| | 90—111 | 25 | 0,7299 | 70,8 | 77,6 |
| | 111—141 | 25 | 0,7587 | 65,8 | 72,0 |
| | 141—к. к. | 25 | 0,8013 | 56,2 | 65,0 |
| Б-70 | Исходный | 100 | 0,7396 | 70,8 | 72,0 |
| | н. к. —84 | 25 | 0,7090 | 75,8 | 78,0 |
| | 84—95 | 25 | 0,7315 | 70,7 | 74,5 |
| | 95—110 | 25 | 0,7455 | 68,6 | 72,0 |
| | 110—к. к. | 25 | 0,7659 | 62,8 | 67,2 |

1) Gasolines; 2) boiling limits of fractions, °C; 3) quantity of fractions, %; 4) density, g/cm³; 5) octane number; 6) motor method; 7) research method; 8) initial; 9) start of boiling.

line (which boils over at 205°) has an octane number of 56.5; this same gasoline, but boiling over at 190°, has an octane number of 59.4; if it boils over at 160°, the octane number is 64.6.

The octane numbers of the fractions in the catalytic gasolines, as a rule, differ only slightly with respect to one another, and the reduction of the end-of-boiling temperature has virtually little influence on the antiknock stability of these gasolines. But some catalytic-cracking gasolines, just like direct-distillation and thermal-cracking gasolines, acquire greater antiknock values as the end-of-boiling temperature is reduced.

To raise the antiknock stability of commercial automotive gasolines, high-octane components are sometimes added; we have reference here to the following components: isopentane, alkylate, benzene, toluene, isooctane, etc. They generally do not exceed 10-20% of the gasolines, since the addition of a greater quantity of some hydrocarbon

would change other properties of the gasoline and, in particular, the fractional composition of the gasoline.

Gas-refining products are frequently used in the production of automotive gasolines; we have reference here, for example, to polymer gasoline, the spent butane fraction, and the pentane-amylene fraction [29].

The polymer gasoline is produced through the polymerization of the propene-butene-pentene fraction. This gasoline has a boiling range from 40 to 200° and an octane number of around 85 without the addition of TES [TEL]. The spent butane fraction, after the alkylation process, contains primarily n-butane. In the pure form, this fraction has an octane number of about 95. The butane fraction has a saturated-vapor pressure above 1600 mm Hg, and, therefore, the possibilities of using this fraction as a high-octane component are limited.

The pentane-amylene fraction is left over after the distillation of the light cracking-gas fractions. This fraction has a boiling range from 25 to 110-130° and has an octane number of about 70.

As certain components are added to the gasolines, the octane number of the mixture formed as a result may differ substantially from the arithmetic mean between the octane numbers of the gasoline and the component. Each component has its unique mixing characteristic or, as this is generally called, a mixture octane number (see Chapter 4).

The most effective and economical method of increasing the antiknock stability of automotive gasolines is the addition of antiknock additives to these gasolines (see Chapter 15).

CHEMICAL STABILITY OF AUTOMOTIVE GASOLINES

Prior to their utilization in an engine, automotive gasolines

TABLE 110

Effect of Tar Content in Fuel on Condition and Operational Readiness of Automotive Engines [17]

| 1 Содержание фактических смол, мг/100 мл | 2 Состояние двигателей после 50 час. работы | 3 Возможный пробег автомобилей до появления неисправностей в двигателе, км |
|---|---|---|
| 4 До 10 | 5 Во впускной системе и в цилиндрах отложений нет | 11 Неограниченный |
| 11—15 | 6 Слабые следы отложений на клапанах и стенках впускной трубы | 25 000 |
| 16—20 | 7 Небольшие отложения на стенках впускной трубы, камеры сгорания и клапанах | 16 000 |
| 21—25 | 8 Заметные отложения в узлах системы питания и камере сгорания | 8 000 |
| 26—50 | 9 Значительные отложения на стенках впускной трубы, камеры сгорания и клапанах. Уменьшение сечения впускной трубы на 20—25% | 12 Не более 5000 |
| 50—120 | 10 Большие отложения на стенках узлов системы питания, камеры сгорания и клапанах. Жиклеры, диффузор и дроссель покрыты липкой смолой | Не более 2000 |

1) Actual tar content, mg/100 ml; 2) condition of engine after 50 hours of operation; 3) possible mileage (in km) prior to improper engine operation; 4) below 10; 5) no deposits in intake system and in cylinders; 6) slight traces of deposits on valves and walls of intake tube; 7) small deposits on walls of intake tube, combustion chamber, and valves; 8) noticeable deposits in feed-system units and combustion chamber; 9) substantial deposits on walls of intake tube, combustion chamber, and valves. Cross section of intake tube reduced by 20-25%; 10) large deposits on walls of feed-system units, combustion chamber, and valves. Carburetor jets, diffuser, and throttle covered with sticky tar; 11) unlimited; 12) not over 5000.

must be transported and stored for a given period of time. During this period the most unstable hydrocarbons, on coming into contact with the air, sometimes in the case of high temperatures, begin to become subject to chemical changes resulting in the formation of heavy resinous substances of complex composition.

The utilization of gasolines having a high tar content results in a number of undesirable phenomena associated with the deposition of the substances within the engine.

Such deposits are most intensively formed as the gasoline vaporizes in the intake manifold of the engine. The tar deposits on the walls of the outlet manifold are polymerized through the action of high temperatures and converted into a rough solid layer that is difficult to remove. In the presence of such a layer, the effective cross section of the manifold is reduced and there is a corresponding reduction in the filling of the engine's combustion chamber with combustible mixture. The deposition layer exhibits extremely low thermal conductivity as a result of which the quantity of heat supplied to the combustible mixture is reduced and the fuel-vaporization conditions are impaired. All of this results in a reduction in engine power and economy.

The formation of heavy deposits on the stems and heads of the intake valves blocks normal valve seating, as a result of which the so-called "sticking" of valves takes place. In this case, it becomes impossible to generate any pressure in the combustion chambers, and the engine ceases to function.

In actual automobile operations we have noted cases in which so much tar was deposited in the intake manifold that its cross section was reduced by 70-80% [30]. Special static tests of new automotive engines have been carried out, and these engines were equipped with the intake manifolds from cars that had been driven for more than 100 thousand kilometers. These tests demonstrated that engine power is reduced by 50% as a result of heavy tar deposition in the intake manifold, that there is a substantial impairment of the uniformity of mixture distribution through the cylinders, and that the specific gasoline consumption is increased [30].

When using a gasoline with an increased tar content, we have noted cases in which the engines are brought to a stop as a resul-

the sticking of the intake valves, and we have reference here to cars that had been driven for less than 16 thousand kilometers [31].

The investigations of gasolines exhibiting various tar contents have shown that the possible distance covered by an automobile prior to the occurrence of engine irregularities as a result of deposition depends on the quantity of actual tars in the gasoline (Table 110).

TABLE 111

Elementary Composition of Tars in Gasoline and of Deposits in Intake Manifold of Engine [32]

| 1 Элементы | 2 Смолы в бензине, % вес. | 3 Отложения в двигателе, % вес. |
|---|---|---|
| 4 Углерод | 72,2 | 75,7 |
| 5 Водород | 7,6 | 8,7 |
| 6 Кислород | 15,5 | 15,4 |
| 7 Сера | 1,5 | 0,2 |
| 8 Азот | 0,15 | — |
| 9 Отношение углерода к водороду | 9,5 | 8,7 |

1) Elements; 2) tars in gasoline, % by weight; 3) engine deposits, % by weight; 4) carbon; 5) hydrogen; 6) oxygen; 7) sulfur; 8) nitrogen; 9) carbon-to-hydrogen ratio.

Commercial gasolines and their components differ in their tendency to form deposits in the intake system. The greatest quantity of deposits is produced by thermal-cracking gasoline, and the least is produced by direct-distillation gasoline.

In connection with the disruptions of normal engine operation, associated with the formation of tar deposits, the industrial specifications for automotive gasolines restrict the content of actual tars (7 mg/100 ml for A-66 gasoline and 5 mg/100 ml for A-72 and A-76 gasolines). These requirements apply at the point of gasoline production, i.e., at petroleum refineries. After transportation and storage of the gasolines, the actual tar content may be increased as

the points of utilization to 20 mg/100 ml for A-66 gasoline and to 10 mg/100 ml for A-72 and A-76 gasolines.

Investigations of the elementary composition of tars separated from gasoline and of deposits removed from the intake manifold of an engine (Table 111) show the apparent similarity between these products.

The process of hydrocarbon oxidation during gasoline storage and transportation is spontaneous and initiated by the oxygen in the air. The conversion of the primary oxidation products into tars has not been thoroughly studied, and the mechanism of the reactions that take place is not clear.

The presence of a certain induction period (lag) was noted in a study of the kinetics of tar formation in gasolines. Initially, tar formation proceeds slowly, then the speed of tar formation picks up, and finally the process is very fast.

Depending on production techniques, automotive gasolines contain hydrocarbons that differ from one another in terms of structure and capacity to enter into chemical reactions, including those reactions which result in the formation of tars.

It follows from a multiplicity of works on the oxidation of individual unsaturated hydrocarbons that the diolefinic hydrocarbons with conjugate double bonds and the mono- and diolefinic hydrocarbons attached to the benzene ring are the least stable. The olefinic hydrocarbons with a double bond at the end of the hydrocarbon chain lend themselves less easily to oxidation than the olefins with the double bond in the middle of the chain. The cyclic olefins are more easily oxidized than the olefins with an open chain. Olefins with a branched skeleton are more easily oxidized than similar hydrocarbons with a straight chain. As the molecular weight of the olefins increases, they become more stable to oxidation. Naphthenic hydrocarbons wi

double bond in the side chain oxidize in the same way as the corresponding olefins.

The nonhydrocarbon impurities in gasolines exert a pronounced effect on the tar-formation process.

Sulfur and sulfur compounds accelerate the tar-formation process in gasolines. Elementary analysis will always show a larger quantity of sulfur compounds in the tars separated from gasoline than there was in the initial gasoline. Each of the sulfur compounds varies in activity in the tar-formation process. Evidently, the mercaptans exert the greatest effect on the formation of tars.

Of the oxygen compounds contained in gasolines, phenol-type compounds are the most significant in the tar-formation process. These compounds, sometimes referred to as "natural inhibitors," retard oxidation and the formation of tars in gasolines.

The chemical stability of commercial automotive gasolines is both a function of the composition and the structure of the hydrocarbon part, as well as of the quantity and nature of the nonhydrocarbon admixtures.

Thermal-cracking gasolines from petroleum crude generally contain substantial quantities of chemically active unsaturated hydrocarbons and exhibit low chemical stability. The duration of the induction period (lag) for the oxidation of thermal-cracking gasolines according to the GOST 4039-48 generally does not exceed 200-250 minutes. Individual thermal-cracking gasoline specimens rich in "natural inhibitors" exhibit a lag of the order of 400-500 minutes. Thermal-cracking gasoline from Ekhabi mazout contains approximately 0.25% phenols and exhibits an oxidation induction lag of 600-800 minutes [33].

Z.A. Sablin and A.A. Gureyev investigated the chemical stability

of thermal-cracking gasolines derived under approximately identical process regimes from Nebit-Dag-petroleum mazouts and from a mixture of Baku petroleums and Tuymazy petroleum (Table 112).

The cracking-gasoline from the Nebit-Dag petroleum exhibited the greatest tendency to oxidation. Within 30 minutes of accelerated oxidation the tar content in this gasoline exceeded 50 mg/100 ml, whereas tar formation in the cracking-gasolines from the Tuymazy and particularly from the Baku petroleums proceeded substantially more slowly under the identical conditions (Fig. 155).

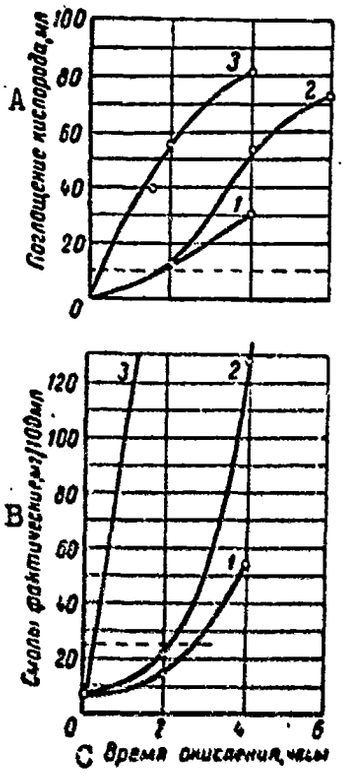


Fig. 155. Chemical stability of various cracking-distillates. 1) From Baku petroleums; 2) from Tuymazy petroleum; 3) from Nebit-Dag petroleum; A) absorption of oxygen, ml; B) actual tars, mg/100 ml; C) time of oxidation, hours.

It is of interest to point out that the total content of unsaturated hydrocarbons (on the basis of the iodine number) in the investigated gasolines is virtually identical (see Table 112) and, consequently, the great tendency of the gasoline from the Nebit-Dag petroleum to oxidize cannot be explained by its increased degree of unsaturation in comparison, for example, with the gasoline from the Baku petroleums, but rather by the various contents of easily oxidized diolefinic hydrocarbons and natural inhibitors in these products. We can see from the data in Table 112 that the greatest quantity of diolefinic hydrocarbons (see the maleic number) is contained in the gasoline from the Nebit-Dag petroleum and that there are virtually no natural antioxidants of the phenol type [4]. The quantity of diolefinic hydrocarbons is smaller by a factor of two

TABLE 112

Chemical Composition and Stability of Thermal-Cracking Gasolines from Various Petroleums

| 1 Происхождение бензина по сырью, взятому для крекинга | 2 Характеристика химического состава | | | 3 Показатели химической стабильности | | |
|---|---|---|---|---|---|---|
| | непредельные углеводороды, % вес. (4) | малеиновое число* г йода/100 г (5) | содержание природных ингибиторов, % триоксибензола** (6) | индукционный период окисления по ГОСТ, мин. (7) | индукционный период окисления (в запаянных ампулах), мин.*** (8) | период сопротивления смолообразованию, мин.*** (9) |
| 10 Из небитдагской нефти | 48 | 7,7 | 13 Отсутствие | 50 | 20 | 20 |
| 11 Из смеси бакинских нефтей | 46 | 4,3 | 0,068 | 190 | 95 | 165 |
| 12 Из туймазинской нефти | 48 | 4,7 | 0,107 | 145 | 90 | 130 |

* The maleic number characterizes the quantity of diolefinic hydrocarbons with conjugate double bonds.

** Natural inhibitors determined in conventional units [34].

*** Quantities calculated according to kinetic oxygen-absorption and tar-formation curves during gasoline oxidation in sealed capsules.

1) Origin of gasoline based on crude employed for cracking; 2) chemical-composition characteristics; 3) chemical-stability indicators; 4) unsaturated hydrocarbons, % by weight; 5) maleic number*, g iodine/100 g; 6) natural-inhibitor content, % of trioxybenzene**; 7) oxidation lag according to GOST, minutes; 8) oxidation lag (in sealed capsules), minutes***; 9) period of resistance to tar formation, minutes***; 10) from Nebit-Dag petroleum; 11) from a mixture of Baku petroleums; 12) from Tuymazy petroleum; 13) absent.

in the Baku gasoline and contains a substantial quantity of phenol antioxidants.

Catalytic-cracking and particularly catalytic-reforming gasolines exhibit higher chemical stability than do thermal-cracking gasolines.

The duration of the induction period for the oxidation of a gasoline produced by single-stage catalytic cracking of gas-oil fractions ranges from 800 to 1200 minutes.

If a rather heavy crude is employed for the cracking, the chemical stability of the gasoline is reduced. In the case of the catalytic

cracking of mazout under severe conditions, a low-stability gasoline is formed, and this product exhibits an induction period of less than 60 minutes. A gasoline of this type cannot serve as a component for automotive gasoline and it is enriched by purification.

Catalytic-reforming gasolines contain negligible quantities of unsaturated hydrocarbons and exhibit an oxidation lag in excess of 1000 minutes. In terms of stability such gasolines are virtually equivalent to direct-distillation gasolines.

Consequently, the chemical stability of commercial automotive gasolines is a function of the properties and quantity of components in the composition [of these gasolines]. To increase the chemical stability, petroleum refineries add special antioxidant additives (see Chapter 17) to the gasolines. At the present time the narrow fractions of wood tar (wood-tar antioxidant) are used to stabilize automotive gasolines, as are phenols from the tar waters of coal semicoking (antioxidant FCh-16), and the synthetic antioxidant – n-oxydiphenylamine.

Under the actual conditions prevailing in the storage of automotive gasolines, the chemical stability of the latter may differ from the stability determined by oxidation in the bomb. The duration of gasoline storage depends in great measure on the storage conditions. By storage conditions we mean primarily such factors as the storage temperature, the presence of nonferrous metals (in contact with the gasoline), the presence of water, the fill factor, the number of times the gasoline is pumped, etc.

With an increase in the gasoline-storage temperature by $10^{\circ}$, the tar-formation process is accelerated by a factor of approximately two. The permissible gasoline storage times under the conditions prevailing in the southern climatic zone are always lower than in the

central and northern zones.

Nonferrous metals act as catalysts in the oxidation of the gasolines. In the presence of such metals, the oxidation of the hydrocarbons in the gasoline and tar formation are substantially accelerated. For example, when gasolines are stored in automobile fuel tanks (where the gasoline comes into contact with a brass pickup tube and a brass filter screen) tar formation takes place much more rapidly than in drums of equal capacity, but not made of nonferrous metal. The type of internal fuel-tank coating has a substantial effect on the rate of tar formation in gasolines (Table 113).

TABLE 113

Effect of Inner Tank Coating on Tar Formation in A-72 Gasoline During Storage

| 1 Характер внутреннего покрытия бака | 2 Содержание фактических смол (в мг/100 мл) при хранении | | |
|---|---|---|---|
| | 3 исход-ные | 4 9 месяцев | 5 14,5 месяца |
| 6 Бак освинцованный на 150 л | 4 | 8 | 33 |
| | 4 | 10 | 31 |
| 7 Бак бакелитированный на 150 л | 4 | 10 | 17 |
| | 4 | 8 | 15 |
| 8 Бак бакелитированный на 60 л | 4 | 5 | 8 |
| | 4 | 6 | 11 |

1) Type of inner tank coating; 2) content of actual tars (in mg/100 ml) during storage; 3) initial; 4) 9 months; 5) 14.5 months; 6) lead lined 150 liter tank; 7) bakelited 150 liter tank; 8) bakelited 60 liter tank.

A lead coating on the inside surface of a tank causes accelerated tar formation during gasoline storage.

Tar water, which accelerates tar formation (Table 114), at times accumulates in gasoline storage tanks.

The free access of the oxygen from the air to the surface of the gasoline enhances accelerated tar formation during storage. In this connection, a fuel contained in a hermetically sealed tank

TABLE 114

Effect of Water on Tar-Formation Process in Gasoline

| 1 Условия хранения | 2 Содержание фактических смол (в мг/100 мл) при хранении | | | |
|---|---|---|---|---|
| | 3 исходные | 4 1 месяц | 5 3 месяца | 6 6 месяцев |
| 7 Бензин без воды . . . . . | 4 | 4 | 6 | 8 |
| 8 Бензин с водяной подушкой | 4 | 6 | 10 | 22 |

1) Storage conditions; 2) content of actual tars (in mg/100 ml) during storage; 3) initial; 4) 1 month; 5) 3 months; 6) 6 months; 7) gasoline without water; 8) gasoline with water cushion.

TABLE 115

Effect of Hermetic Sealing of Car Tank on Process of Tar-Formation in Gasoline

| 1 Условия хранения | 2 Содержание фактических смол (в мг/100 мл) при хранении | | | | |
|---|---|---|---|---|---|
| | 3 исходные | 4 1 месяц | 5 2 месяца | 6 3 месяца | 7 4,5 месяца |
| 8 Топливный бак автомобиля ЗИС-150 с обычной пробкой | 2 | 4 | 8 | 21 | 28 |
| 9 Топливный бак автомобиля ЗИС-150 с герметичной пробкой . . . . . | 2 | 4 | 4 | 4 | 16 |

1) Storage conditions; 2) content of actual tars (in mg/100 ml) during storage; 3) initial; 4) 1 month; 5) 2 months; 6) 3 months; 7) 4.5 months; 8) fuel tank of ZIS-150 automobile, with standard cap; 9) fuel tank for ZIS-150 automobile, with hermetic-sealing cap.

oxidizes more slowly (Table 115).

When gasoline is stored in an incompletely filled volume, a greater surface of the fuel comes into contact with the air per unit fuel weight and thus the oxygen has freer access to the gasoline and the formation of tars is speeded up (Table 116).

With frequent pumping, the gasoline becomes saturated with the oxygen from the air and rapidly oxidizes, thus forming tars.

Consequently, if proper conditions are provided the permissi-

TABLE 116

Effect of Fill Factor on Intensity of Tar Formation in Gasoline

| 1 Условия хранения | 2 Содержание фактических смол (в мг/100 мл) при хранении | | | |
|---|---|---|---|---|
| | 3 исход-ные | 4 3 месяца | 5 6 месяцев | 6 10 месяцев |
| 7 В емкости, заполненной на 100% | 4 | 6 | 8 | 18 |
| 8 В емкости, заполненной на 25% . . | 4 | 12 | 36 | 78 |

1) Storage conditions; 2) content of actual tars (in mg/100 ml) during storage; 3) initial; 4) 3 months; 5) 6 months; 6) 10 months; 7) in 100% filled tank; 8) in 25% filled tank.

storage time for automotive gasolines can be substantially increased and better grades of fuel are made available for use in engines.

CORROSION AGGRESSIVENESS OF AUTOMOTIVE GASOLINES

The hydrocarbons contained in the composition of a fuel exert no corrosive effect on the metals with which the gasolines come into contact during storage, transportation, or use in engines. The corrosive aggressiveness of gasolines is caused by the nonhydrocarbon admixtures present and primarily by the sulfur and oxygen-bearing compounds as well as by water-soluble acids and alkalis.

The water-soluble acids and alkalis are chance gasoline impurities. Of this group of corrosive agents, the presence of the alkali NaOH is most frequently detected. Present-day techniques for the production of automotive-gasoline components call for the flushing of these components with an 8-12% alkali solution. After alkalization, the gasolines are flushed with water; if inadequately flushed, traces of alkali may remain within the gasolines.

The presence of sulfuric-acid traces in gasolines is virtually excluded, since sulfuric-acid purification of gasoline distillates is not employed in our refineries.

Water-soluble acids and alkalis may enter the gasoline if the

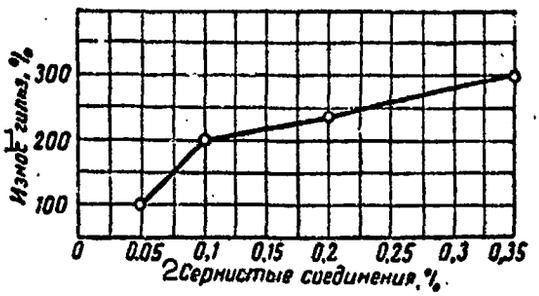


Fig. 156. Effect of quantity of sulfur compounds in gasoline on cylinder-housing wear in the zone of maximum wear. 1) Housing wear, %; 2) sulfur compounds, %.

tanks, the fuel lines, etc., have not been sufficiently cleaned. This results in the intense corrosion of the metals and the presence of these acids and alkalis in automotive gasolines is therefore intolerable.

Oxygen-bearing compounds, unlike the water-soluble acids and alkalis, are always present in some quantity in gasolines. These may come into a gasoline from the petroleum or the distillates during the refining process in the form of naphthenic acids. Moreover, these compounds are formed during the oxidation of the more unstable hydrocarbons of the gasoline during storage and transportation. Among the hydrocarbon-oxidation products the peroxide compounds and acids exhibit the most corrosive properties. The corrosion of metals by peroxide compounds has not been thoroughly studied.

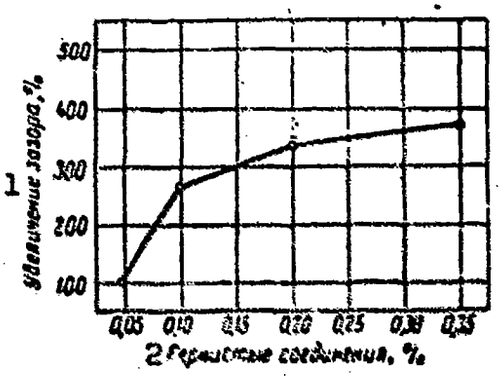


Fig. 157. Effect of quantity of sulfur compounds in gasoline on an increase in the seal clearance of the first compression piston ring. 1) Increase in clearance, %; 2) sulfur compounds, %.

Organic acids which form in the oxidation of the hydrocarbons are more powerful agents than those acids which come into the gasoline during the refining processes. They do not affect aluminum, have little effect on steel and cast iron, but they corrode nonferrous metals, primarily lead and zinc.

The removal of acidic oxygen-bearing compounds from the gasolines is an extremely complex undertaking; therefore, in view of their relatively weak corrosive effect

a certain quantity of organic acids is permitted in gasolines.

Sulfur compounds in gasolines, from the standpoint of their corrosive aggressiveness, are divided into active (elementary sulfur, hydrogen sulfide, and the mercaptans) and the inactive (sulfides, disulfides, polysulfides, thiophanes, thiophenes, etc.) (see Chapter 9).

The active sulfur compounds are extremely powerful corroding agents and, therefore, their presence in commercial automotive gasolines is intolerable. To remove the active sulfur compounds, petroleum refineries employ the practice of flushing the gasoline distillates with an alkali solution. This means that the elementary sulfur and the hydrogen sulfide are completely removed from the fuel, and the mercaptans are only partially removed.

The extent to which these active sulfur compounds have been removed is checked by running a test on a copper plate. The contention here is that if the gasoline passes the copper-plate test, it will not corrode the metals that come into contact with the gasoline under conditions of storage and utilization.

The inactive sulfur compounds that are present in automotive gasolines cause virtually no corrosion of the metals of which the tanks, manifolds, and component parts of the fuel system of an engine are made.

The division of the sulfur compounds in gasolines into active and inactive categories is valid only for the periods of storage and transportation. During the process of the combustion of the fuel-air mixture all sulfur compounds form products that are extremely corrosive: sulfurous anhydride $SO_2$ and sulfuric anhydride $SO_3$. It has been established experimentally that with an increase in the quantity of sulfur compounds in a gasoline there is an increase in

the wear of engine component parts that can be attributed to corrosion [9].

Figures 156 and 157 show changes in the extent of cylinder-housing wear in the zone of maximum wear and the increase of the clearance in the seal of the first compression piston ring as a function of the sulfur content in the gasoline [8]. The resultant data indicate that even small quantities of sulfur compounds produce a pronounced increase in the corrosive wear of the component parts.

The relationship between $SO_2$ and $SO_3$ in the products of combustion has a substantial effect on the corrosion of engine component parts. This relationship is not constant and depends on many factors. If in the presence of $SO_2$ the wear of the rings increases by a factor of 4, the $SO_3$ introduced into the engine in a quantity equal to 1/3 of the $SO_2$ will increase ring wear by a factor of 40 [24].

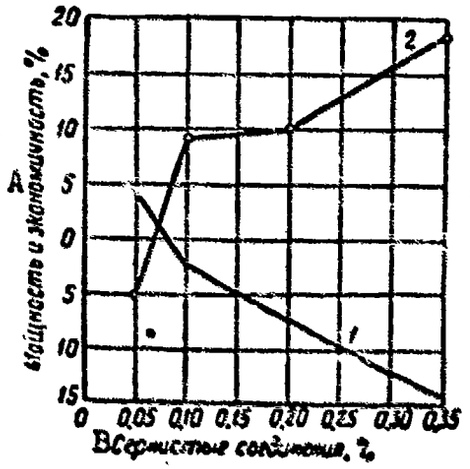


Fig. 158. Effect of quantity of sulfur compounds in gasoline on power and economy of engine after 220 hours of operation. 1) Power; 2) specific consumption according to external characteristics; A) power and economy, %; B) sulfur compounds, %.

Corrosive wear of engine component parts when sulfur-containing automotive gasolines are used brings about a reduction in the power and economy indicators of the car. Figure 158 shows the change in power and economy of an automotive engine after 220 hours of operation on a gasoline with various sulfur contents. In operations on a low-sulfur gasoline the power and economy of the engine increase slightly after 220 hours (by 4-5%). The power of the engines operating on gasolines containing 0.1%, 0.2%, and 0.357% of sulfur fell, respectively, 3%, 7.5% and 14.5% and exhibited a pronounced

reduction in engine economy [8]. When the engines were dismantled it was noted that the tightness of the valve fit had been disrupted through spot corrosion of the bevels and seats of the valves. An increase in the flowthrough section of the carburetor jets, attributable to corrosion, was also noted, and this resulted in an increase in the output of the jets, thus disrupting the normal regulation of the engine fuel systems.

The circumstances noted above are associated with the utilization of sulfur automotive gasolines and make it necessary to maintain strict controls on the content of sulfur compounds in gasolines.

AUTOMOTIVE GASOLINES ABROAD

The physicochemical and operational properties of automotive gasolines, produced in any country, are functions of the over-all level of development in the petroleum-refining industry of that

TABLE 117

Compression Ratio in American and European Engines

| 1 Страны | 2 Степень сжатия двигателей | | |
|---|---|---|---|
| | 3 наибольшая | 4 наименьшая | 5 средняя |
| 6 США | 10,50 | 7,80 | 9,38 |
| 7 Англия | 8,30 | 6,46 | 7,75 |
| 8 Франция | 7,80 | 6,50 | 7,09 |
| 9 Италия | 8,40 | 7,00 | 7,33 |
| 10 Западная Германия | 8,10 | 6,00 | 6,82 |

1) Countries; 2) engine compression ratios; 3) greatest; 4) least; 5) average; 6) USA; 7) Great Britain; 8) France; 9) Italy; 10) West Germany.

country and the condition of the automotive pool in operation.

The automotive pool of the USA is substantially different from the automotive pool of European countries.

The average power produced by American automotive engines in

1958 was 259 hp and the displacement exceeded 4.0 liters. More than 80% of all American engines are 4-cycle water-cooled V-8 engines.

As a rule, European automotive engines are less highly tuned and therefore last longer. Their displacement does not exceed 1.5 liters. Basically European cars employ water- (sometimes air-) cooled in-line 4-cylinder 4-stroke engines.

All countries are constantly increasing the compression ratios of the automotive engines they produce. Table 117 shows data on compression ratios in standard 1958 automotive engines. It is assumed that by 1962 the maximum compression ratio in standard automotive engines produced in Western Europe will be 9.3, and 11.7 in the USA.

Passenger automobiles in the USA and Europe use gasoline engines; only 3% of the automobiles in West Germany operate on diesel fuel, and 5% of the automobiles in Italy operate with gas-driven engines.

Among the European automobiles, those exhibiting the greatest fuel economy are in the greatest demand and this is explained by the relatively high cost of gasoline in European countries.

Low-displacement European automobiles provide for lower fuel consumption per 100 km than do American cars, although in terms of specific consumption per kilometer-ton they are almost the same (Table 118).

Individual companies, following their own technical specifications, produce automotive gasolines in the capitalist countries. As a rule, national standards for automotive gasolines do not exist.

The automotive gasolines produced by various companies in the USA exhibit a wide range of octane numbers. All gasolines are conventionally divided into two basic grades - premium and regular. This classification of gasolines is becoming more common in Europe.

The average octane number of regular USA gasoline in 1960 was

TABLE 118

Gasoline Consumption in American and European Automobiles [6]

| 1 Страны | 2 Средний расход бензина при скорости движения 80 км/час | |
|---|---|---|
| | 3 л/100 км | 4 л/100 т км |
| 5 США | 12.9 | 8.3 |
| 6 Англия | 8.0 | 8.6 |
| 7 Франция | 7.4 | 9.3 |
| 8 Италия | 5.9 | 9.1 |
| 9 Западная Германия | 8.0 | 8.6 |

1) Country; 2) average gasoline consumption at a speed of 80 km/hr; 3) l/100 km; 4) l/100 t km; 5) USA; 6) Great Britain; 7) France; 8) Italy; 9) West Germany.

TABLE 119

Quality of Automotive Gasolines and Needs of Automotive Pools in a Number of Countries (According to Data for the Year 1958) [6]

| 1 Показатели | 2 США | 3 Англия | 4 Франция | 5 Италия | 6 Западная Германия |
|---|---|---|---|---|---|
| 7 Октановые числа по исследовательскому методу, требуемые для парка: | | | | | |
| 25% | 83 | 78 | 78 | 80 | 79 |
| 50% | 88 | 84 | 82 | 81,5 | 83 |
| 75% | 93 | 90 | 87 | 84 | 86,5 |
| 95% | 98,5 | 95,5 | 92,5 | 92 | 91,5 |
| 8 Средние октановые числа по исследовательскому методу: | | | | | |
| 9 регулярный бензин | 91,5 | 92 | 92 | 92,5 | 92 |
| 10 премиальный бензин | 98,5 | 96 | 93 | 93 | — |
| 11 суперпремиальный бензин | 102 | 100 | — | — | — |
| 12% автомобильного парка, удовлетворяемый бензином: | | | | | |
| 13 регулярным | 67 | 41 | 50 | 50 | 52 |
| 14 премиальным | 95 | 96 | 94 | 88 | — |
| 15 суперпремиальным | 99 | 99 | — | — | — |

1) Indicators; 2) USA; 3) Great Britain; 4) France; 5) Italy; 6) West Germany; 7) research-method octane numbers required for automotive pool; 8) average research-method octane numbers; 9) regular gasoline; 10) premium gasoline; 11) superpremium gasoline; 12) % of automotive pool satisfied with the following gasolines; 13) regular; 14) premium; 15) superpremium.

about 85 units by the motor method and about 93 units by the research method. Premium gasoline had an octane number of 90 and 100 units, respectively.

To determine the relationship between the requirements of automotive engines in terms of gasoline quality and the actual quality of the gasoline both the USA and Europe regularly conduct extensive tests on stock models of automobiles in operation. Table 119 shows the actual quality of commercial gasolines and the requirements of the automotive pools in the USA and Europe with respect to antiknock properties of fuels, evaluated in terms of octane numbers determined against primary reference fuels.

The automotive gasolines in the USA differ from the commercial gasolines in our country primarily in terms of antiknock properties. The high antiknock values of USA gasolines are attained by the utilization of products of catalytic processes in the composition of commercial fuels and the mandatory introduction of ethyl fluid.

The utilization of ethylated automotive gasolines abroad is permitted in all cities. The permissible TES [TEL] content in the automotive gasolines of the USA and the countries of Europe (Table 120) is substantially higher than in the USSR.

In recent years certain American companies have started the production of so-called supergasolines having octane numbers above 100 units (by the research method).

The production of gasolines with high antiknock values in the USA required substantial investigation in order to determine the economic feasibility of raising the compression ratios of automotive engines in connection with the expenditures involved in the production of high-octane gasolines.

Formerly an increase in octane numbers for automotive gasolines

TABLE 120

Permissible and Actual Tetraethyllead Content in European and American Automotive Gasolines (g TES/kg)

| 1 Страна | 2 Премиальный бензин | | 3 Регулярный бензин | |
|---|---|---|---|---|
| | 4 допустимое содержание | 5 среднее фактическое содержание | 6 допустимое содержание | 7 среднее фактическое содержание |
| 8 США | 1,79 | 1,56 | 1,79 | 1,24 |
| 9 Англия | 1,79 | 0.77 | 1,79 | 0,84 |
| 10 Франция | 1,13 | 0,54 | 1,13 | 0,84 |
| 11 Италия | 1,38 | 1,38 | 1,13 | 1,08 |
| 12 Западная Германия | 1,38 | 0,59 | 1,38 | 1,13 |

1) Country; 2) premium gasoline; 3) regular gasoline; 4) permissible content; 5) average actual content; 6) permissible content; 7) average actual content; 8) USA; 9) Great Britain; 10) France; 11) Italy; 12) West Germany.

in the USA was attained by using industrial processes which raised the yield of gasoline from petroleum (for example, cracking processes), and therefore the cost of gasoline was increased only slightly.

To increase the octane numbers of contemporary automotive gasolines special processes are needed (isomerization, sharp rectification, etc.), whose application involves an increase in the cost of gasolines. The utilization of higher-octane gasolines in automotive engines must yield an economic effect which would justify the price rise in the gasoline.

The calculations and investigations that have been carried out showed that minimum fuel expenditures are attained with existing gasoline-production techniques with a fuel octane number of 98.5. This is an average for all petroleum refineries in the USA and will not vary from refinery to refinery by more than 1 unit. With the increase in the octane number from 94 units (the 1958 level) to 98.5 units, approximately 0.5 liters of gasoline or more than 3 cents were economized per each 100 km that a single car was driven. The

TABLE 121

Average Fractional Composition of Premium Automotive Gasolines in Europe and the USA (for Analogous Climate Zones)

| 1 Показатели | 2 США | 3 Англия | 4 Франция | 5 Италия | 6 Западная Германия |
|---|---|---|---|---|---|
| 7 Фракционный состав (перегоняется при температуре), °С: | | | | | |
| 8 н. к. | 33 | 32 | 36 | 34 | 36 |
| 10% | 49 | 54 | 54 | 54 | 54 |
| 50% | 99 | 99 | 99 | 93 | 93 |
| 90% | 163 | 166 | 157 | 154 | 154 |
| 9 к. к. | 202 | 199 | 188 | 182 | 193 |
| 10 Давление насыщенных паров, мм рт. ст. | 520 | 465 | 494 | 465 | 442 |

1) Indicators; 2) USA; 3) Great Britain; 4) France; 5) Italy; 6) West Germany; 7) fractional composition (distilled at the following temperature), °C; 8) start of boiling; 9) end of boiling; 10) saturated-vapor pressure, mm Hg.

economy resulting from the increase in the engine compression ratio and the increase of the octane number to 98.5 amounts annually to more than 2 million tons of gasoline, or approximately a quarter of a billion dollars, for the entire automotive pool of the USA [26].

Economic calculations of this type are an aid in the selection of compression ratios for new automotive-engine designs and in the determination of the required antiknock values of the automotive gasolines being produced. However, the car-manufacturing companies of the capitalist countries do not always base their decisions as to the production of particular cars on calculations of the economic feasibility of production or on such considerations as the conservation of the national fuel reserve. Fierce competition, the race for the latest "fashion," advertising considerations, and other factors frequently force car-manufacturing companies in the USA to produce engines that admittedly develop excessive power, operate at a "superhigh" compression ratio, etc. Cars with such engines are not

marked by their economy of operation and long life.

Now let us say several words about other physicochemical properties of foreign gasolines. The automotive gasolines of the USA and Europe are quite similar to one another in terms of fractional composition (Table 121).

We can see from Table 121 that the American and European gasolines contain a large quantity of light fractions, and this imparts good starting properties to these gasolines.

The automotive gasolines of the USA differ in terms of fractional composition on the basis of the climatic zones and time of year in which they are used. According to one of the most commonly used specifications for automotive gasolines issued by the American Society for Testing Materials (ASTM), the entire territory of the USA is divided into three climatic belts. Provision is made for the production of a gasoline of specific fractional composition for each climatic belt. Moreover, in each climatic zone, depending on the time of year, gasolines of the corresponding fractional composition are produced.

The chemical stability of American automotive gasolines at the present time is not standardized, since the highly effective synthetic antioxidant additives that are in use provide for high chemical stability on the part of the commercial gasolines.

The permissible content of sulfur compounds in American gasolines is quite high – up to 0.25%. The utilization of anticorrosion additives makes it possible to avoid increased engine wear when using gasolines that contain sulfur.

To improve the operational characteristics of gasolines, widespread use is made in the USA of antiscaling, antiicing, and certain similar additives (see Chapter 14).

Certain of the countries that do not have adequate petroleum reserves produce automotive gasolines from coal, gases, etc. A series of auxiliary requirements (on the basis of certain indicators) is generally imposed on such gasolines. For gasolines produced from coal, for example, the requirements are based on low-temperature properties.

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## Chapter 18

## DIESEL FUELS

Different types of fuels are used in accordance with the speed at which the engine runs. High-speed diesels use kerosene-, gas-oil-, and solar fractions produced by direct distillation of petroleum, while slow diesels use heavier distillates, as well as the residual fractions of direct petroleum distillation or thermal cracking. More recently, kerosene- and gas-oil fractions obtained by catalytic and thermal cracking of petroleum products have come into use as diesel fuels for high-speed diesels.

In a diesel engine, the fuel is injected directly into the cylinder, where it self-ignites without any outside ignition source, under the influence of the high temperature and pressure of the air compressed in the cylinder. The fuel-air mixture of a diesel engine is prepared directly in its cylinder, to which the fuel is fed in liquid form.

For normal combustion of fuel in the engine, it is necessary, firstly, that it have time for complete evaporation in the cylinder and, secondly, that the proportions of fuel and air be as uniform as possible over the entire volume of the cylinder. These two conditions are determined by both the perfection of the injection apparatus and the design of the engine's combustion chamber, as well as by the properties of the diesel fuel (fractional composition, viscosity, density, and so forth).

The high temperatures and pressures in the cylinder of the diesel engine that are required for self-ignition of the fuel are attained by use of a high compression ratio (as high as 17–20).

The injection apparatus insures extremely fine atomization of the fuel in the engine's cylinder. The special nozzles used for this purpose have holes of extremely small diameter (0.15 – 0.2 mm) and inject the fuel at very high pressures (up to 1500 kg/cm$^2$). This pressure is created and the fuel supply to the nozzle is regulated by the fuel pump. The slightest occlusion of the nozzle openings on the inside by mechanical impurities originating from the fuel, or from the outside by scale formed on combustion of low-grade fuels is sharply detrimental to fuel atomization or cuts off the fuel supply entirely.

To protect the nozzles from plugging of their holes by mechanical impurities, coarse and fine filters are installed in the fuel system of any diesel engine. A schematic diagram of the fuel system of the NATI KD-35 diesel is shown in Fig. 159.

To ensure normal performance of the injection apparatus, it is necessary that the fuel arrive continuously at the pump, i.e., that it not clog the fuel-system pipe lines; this is a function of the properties of the fuel.

At the present time, there are a number of diesel-engine modifications that differ from one another in combustion-chamber design and in having different mixing efficiencies. The basic types of engines are the antechamber types, in which the fuel is injected not into the main chamber, but into an antechamber provided specifically for this purpose; single-chamber engines, with direct injection of the fuel into the chamber, and engines with swirl chambers in which special vortical air flows are set up with direct injection of the fuel.

Each type of chamber has its advantages and disadvantages. The best as regards mixing efficiency and the stress placed on the connecting-rod and crank mechanism are the antechamber diesels, and the worst from this standpoint are the single-chamber types. However, the single-cham-

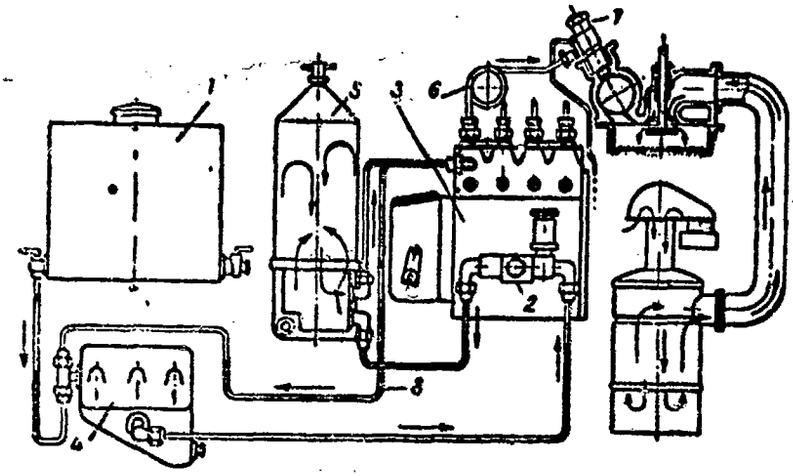

Fig. 159. Schematic diagram of fuel supply to NATI KD-35 diesel. 1) Fuel tank; 2) booster pump; 3) fuel pump; 4) coarse filter; 5) fine filter; 6) line; 7) nozzle; 8) excess-fuel line.

ber engines are superior as regards economy and ease of starting to the swirl-chamber types and especially to the antechamber types.

During recent years, multifuel diesel engines capable of operating on fuels of any fractional and chemical composition ranging from the gasolines to the residual fuels have come into use.

The operating conditions of high-speed diesel engines are not constant. As a rule, low-speed stationary engines operate under a rigorously defined set of conditions.

Consistent with the variable operating conditions of high-speed diesels, their conditions of evaporation, mixing and combustion of the fuels also vary. Consequently, high-speed diesels have very high demands as regards the quality of the fuels that they use.

SPECIFICATIONS SET FORTH FOR DIESEL FUELS

On the basis of the conditions under which the fuel is used in the diesel engine, as well as the conditions of shipping and storage, the following specifications are imposed for a diesel fuel.

1. A diesel fuel must be stable in storage, i.e., it must not undergo any changes in properties during prolonged storage.

2. A diesel fuel must not form deposits in the machine's tank or on the coarse and fine filters, and must also contain no abrasive particles (mechanical impurities).

3. The supply of fuel through the fuel system must be absolutely reliable; hence, a diesel fuel must possess a low initial-crystallization temperature and a low pour point and a definite viscosity.

4. A diesel fuel must not corrode the reservoir, machine tanks and fuel system nor cause any other attrition of the latter.

5. A diesel fuel must not form tar or varnish deposits on the atomizer needles of the nozzles and gum them up.

6. In the injection of the fuel into the engine's cylinder, its atomization must be as thorough as possible and the range of the spray rigidly defined; this is ensured not only by the design sophistication of the fuel apparatus and a certain injection pressure, but also by a certain combination of fuel viscosity with surface tension and density.

7. A diesel fuel must have a short self-ignition lag or a high cetane number.

8. A diesel fuel must not form scale on the nozzles or in the combustion chamber; nor may it cause sticking of the valves or burning of the piston rings.

9. The combustion products must not corrode the various engine components and, and if they enter the crankcase, must not react with the oil to form products that are detrimental to the latter's quality.

In order to satisfy the requirements listed above, a diesel fuel must possess a certain combination of physicochemical properties. Research into the influence exerted by diesel-fuel quality on the operation of high-speed diesels has established optimum values for the phy-

sicochemical properties of a fuel that satisfy the above requirements. It should be noted that with the appearance of new, more highly stressed engines, the specific values of the physicochemical properties of the fuel undergo changes, and specific quality indicators are dropped in favor of new ones.

PROPERTIES OF FUEL THAT ENSURE TROUBLE-FREE PERFORMANCE OF FUEL SYSTEM

Trouble-free operation of a diesel engine's fuel apparatus is determined by the purely physical quality indices of the fuel, its chemical composition, and by the presence of water and mechanical impurities in the fuel.

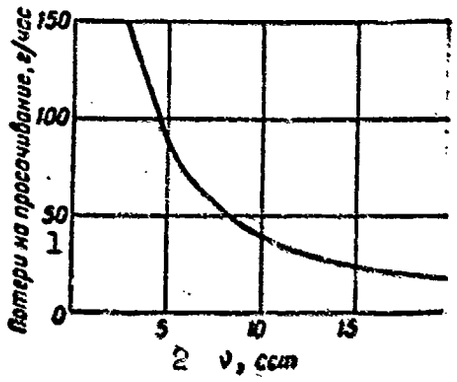


Fig. 160. Relationships between fuel viscosity and quantity of fuel seeping through leaks in pump [1]. 1) Seepage losses, g/hour; 2) ν, cst.

The physical indices of fuel quality, which determine the performance of the fuel apparatus, include viscosity, density and surface tension.

Viscosity is an extremely important operational index to diesel-fuel quality. At a given temperature, it determines the fluidity and ease of transport of the fuel to the nozzle. Fuel viscosity influences the delivery coefficient of the pump and fuel leakage through the gaps in the plunger pairs, as well as the smoothness with which multi-plunger pumps operate. The lower the viscosity of the fuel, the more of it will seep through between the plunger and the sleeve (Fig. 160), and, accordingly, the lower will be the delivery coefficient. Since the fuel itself serves as the lubricant for the plungers of the fuel pump, plunger-pair wear in the fuel pump also depends on its viscosity. As a result of wear, the clearances in the precision-fitted pairs of the pumps and nozzles become larger, and this causes blow-by of the fuel, a drop

TABLE 122

Influence of Fuel Viscosity on Variation of Its Feed Rate in Long-Term Pump Operation [4].

| 1 Время работы, часы | 2 Топливо с $\eta_{20}$=6,14 сст | | 4 Топливо с $\eta_{20}$=2,37 сст | | 5 Топливо с $\eta_{20}$=1,27 сст | |
|---|---|---|---|---|---|---|
| | 3 мл/мин | % | мл/мин | % | мл/мин | % |
| 100 | 72,0 | 100,0 | 59,0 | 100,0 | 58,5 | 100,0 |
| 125 | 68,5 | 95,2 | 54,5 | 92,4 | 53,0 | 90,6 |
| 250 | 62,2 | 86,2 | 47,0 | 79,7 | 43,0 | 73,5 |
| 375 | 58,5 | 81,3 | 42,5 | 72,0 | 37,5 | 64,2 |
| 6 Потеря подачи за 375 час. . . . | 13,5 | 18,7 | 16,5 | 28,0 | 21,0 | 35,8 |

1) Operating time, hours; 2) fuel with $\eta_{20}$ = 6.14 cst; 3) ml/min; 4) fuel with $\eta_{20}$ = 2.37 cst; 5) fuel with $\eta_{20}$ = 1.27 cst; 6) feed loss over 375 hours.

in delivery rate, lowered injection pressure, and a loss in the power developed by the engine. The lower-limit viscosity of a diesel fuel – that which guarantees against excessively rapid plunger-pair wear – depends on the design features of the fuel apparatus and the conditions under which it is operated. Thus, for the fuel apparatus used with the YaAZ-204 engine, a drop in fuel viscosity from 6.0 to 2 cst (at 20°) has no effect on plunger wear, as will be seen from the data presented below [3].

| 1 Вязкость топлива при 20°, сст | 2 | 3 | 6 | 7 | 17 | 140 |
|---|---|---|---|---|---|---|
| 2 Средний износ плунжеров за 550 час. работы, мк . . . . . | 1,5 | 2,0 | 1,5 | 2,3 | 4,5 | 3,8 |

1) Fuel viscosity at 20°, cst; 2) average plunger wear after 550 hours of operation, μ.

At the same time, a drop in fuel viscosity from 6.14 to 2.37 cst causes more rapid wear of the fuel apparatus of the D-6 engine. This is illustrated by the data of Table 122.

In view of the fact that the fuel's viscosity increases with in-

creasing pressure for engines having fuel systems operating at very high pressure, the minimum fuel-viscosity value determined at 20° and atmospheric pressure will be lower. Thus, for the YaAZ-204 (atomizing pressure up to 1500 kg/cm$^2$), no increase in wear of plunger pairs is observed even in cases where the fuel viscosity is only 1.25 – 1.3 cst.

In combination with density and surface tension, viscosity exerts an essential influence on the extent to which the fuel is atomized and the range of the spray. The fuel is atomized better at low viscosities, but the spray range diminishes. With increasing viscosity, the depth of penetration of the jet does increase, but the extent of atomization drops sharply and drop size is larger (Fig. 161). As a result, the conditions for fuel vaporization deteriorate, complete combustion is not achieved, the specific fuel consumption rises and we observe a smoky exhaust. The optimum viscosity range, which guarantees normal atomization of the fuel, depends on the design of the fuel apparatus and the combustion chamber.

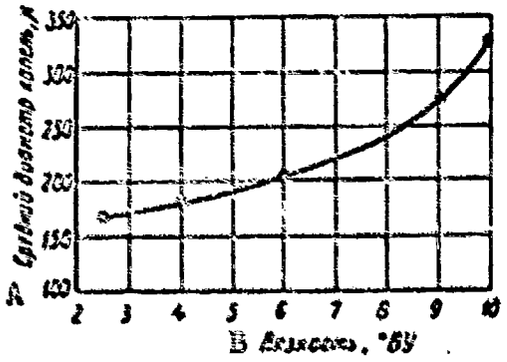


Fig. 161. Influence of fuel viscosity on fineness of atomization. A) Average drop diameter, μ; B) viscosity, °VU.

The surface tension of the fuel exerts considerable influence on thoroughness of atomization (Table 123). With increasing surface tension, the average drop diameter increases.

The density of the fuel also exerts a certain influence on the range of the spray. Thus, when an engine was switched from a fuel having a density of 0.848 to a fuel with a density of 0.873, the range of the spray increased by 20% [2].

The influence of the chemical composition of the diesel fuel on the dependability of the fuel apparatus is determined by the presence, in

TABLE 123

Fuel-Drop Diameter as a Function of Surface Tension (I.F. Larchenko)

| 1 Топливо | Поверхностное натяжение, 2 эрг/см² | 3 Средний диаметр капли, мк |
|---|---|---|
| 4 Из сураханской нефти: | | |
| 5 дистиллят, широкая фракция . . | 28,92 | 17,04 |
| 6 дистиллят, фракция 300—350° . . | 29,68 | 22,55 |
| 7 Из бибп-эйбатской нефти: | | |
| 8 дистиллят, широкая фракция . . | 29,53 | 20,21 |
| 9 то же . . . . . | 27,48 | 16,30 |

1) Fuel; 2) surface tension, ergs/cm$^2$; 3) average drop diameter, μ; 4) from Surakhany petroleum; 5) broad-fraction distillate; 6) distillate, 300 - 350° fraction; 7) from Bibi-eybat petroleum; 8) broad-fraction distillate; 9) same.

the fuel, of corrosively active compounds and compounds capable of undergoing changes at temperature to form tarry compounds, as well as the presence of other compounds that are aggressive toward the individual units of the fuel apparatus.

The primary corrosively active substances are acidic oxygen-containing compounds that get into the fuel during production (naphthenic acids) or form in it during storage as a result of oxidation, as well as certain sulfur compounds (hydrogen sulfide, elementary sulfur and mercaptans) present in fuels produced from high-sulfur petroleums. The influence of the above compounds on corrosion of the fuel apparatus is described in Chapter 12.

When diesel engines are operated primarily on high-sulfur diesel fuels and diesel fuels containing products of catalytic and particularly thermal cracking, we observe cases in which the nozzle-atomizer needles become gummed up, with the result that the supply of fuel by the nozzle is cut off completely or the fuel is not atomized, but fed into the cylinder in a stream. Atomizer-needle sticking results from the

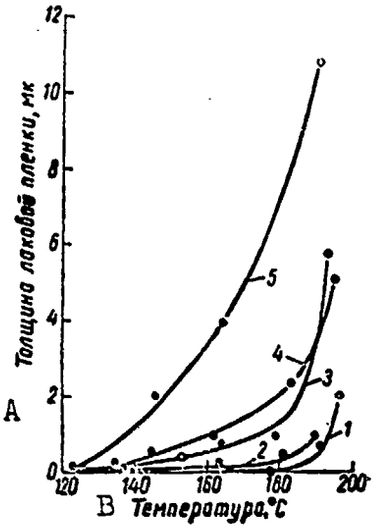


Fig. 162. Influence of temperature on tarring of nozzle-atomizer needles [8]. 1) DZ low-sulfur diesel fuel; 2) diesel fuel containing 1.16% of sulfur but not containing mercaptans; 3) catalytic diesel fuel; 4) diesel fuel containing 0.3% of sulfur, including 0.1% of mercaptan sulfur; 5) diesel fuel produced by hydrogenation of coal tar. A) Thickness of varnish film, μ; B) temperature, °C.

formation of tarry or varnish deposits on the needles. The basic factor determining the tendency of the fuels to form deposits on nozzle-atomizer needles is temperature. Figure 162 shows the influence of temperature on the thickness of the varnish film formed on the nonworking surface of a nozzle-atomizer needle in operation on diesel fuels of various origins. The experiments were conducted on a special nozzle bench that simulated the fuel system of a diesel engine. As will be seen from the curves of Fig. 162, the thickness of the varnish film increases in operation on all fuels with rising temperature. The lowest temperature at which a varnish film forms on the atomizer needle and the rate at which it forms with increasing temperature depend on the chemical composition of the fuel. It has been shown by research that the formation of tarry or varnish deposits on atomizer needles is the result of oxidative-polymerization processes that take place at temperature. The mercaptans, oxygen compounds and unsaturated hydrocarbons present in a diesel fuel are most susceptible to oxidative polymerization. As will be seen from the data of Table 124, the temperature at which atomizer-needle tarring begins rises sharply as a result of removal of the mercaptans and oxygen compounds from diesel fuels.

However, not all mercaptans and oxygen compounds undergo oxidation to equal degrees with formation of tarry deposits. The most strongly

TABLE 124

Influence of Mercaptans and Oxygen Compounds on Tarring of Nozzle-Atomizer Needles [8]

| 1 Топливо | 2 Толщина пленок на иглах (в мк) при температурах, °С | | | | | | 3 Температура начала осмоления, °С |
|---|---|---|---|---|---|---|---|
| | 190—195 | 180—151 | 170—178 | 147—151 | 135—140 | 124—132 | |
| 4 Дизельное топливо, содержащее 0,0129% меркаптановой серы | 5,0 | 2,25 | 1,0 | 0.75 | 6 Нет | Нет | 149 |
| 5 То же после удаления меркаптанов | 0,75 | Нет | Нет | Нет | » | » | 192 |
| 7 Дизельное топливо, содержащее 0,008% меркаптановой серы | 1,0 | 0,5 | 8 Следы | » | » | » | 166 |
| 9 То же после удаления меркаптанов | 0,5 | Нет | Нет | » | » | » | 190 |
| 10 Дизельное топливо каталитического крекинга | 1,5 | 0,75 | 0,625 | 0,25 | — | 0,25 | 126 |
| 11 То же после удаления смол | 1,0 | Нет | Нет | Нет | Нет | Нет | 192 |

1) Fuel; 2) thickness of films on needles (in μ) at temperatures of °C; 3) temperature of onset of tarring, °C; 4) diesel fuel containing 0.0129% of mercaptan sulfur; 5) same, after removal of mercaptans; 6) none; 7) diesel fuel containing 0.008% of mercaptan sulfur; 8) traces; 9) same, after elimination of mercaptans; 10) catalytic-cracking diesel fuel; 11) same, after removal of tars.

inclined to formation of deposits are the aromatic mercaptans and highly oxidized oxygen compounds (Fig. 163). It should be noted that the oxygen compounds present in diesel fuel differ only slightly in molecular weight from the hydrocarbons composing the diesel fuel [9]. This indicates that high-molecular weight compounds are not formed in diesel fuels during storage.

Figure 163 shows the quantities of deposit formed during three months' storage of catalytic gas oil at 40° with addition of aromatic mercaptans to it [10].

The degree to which the unsaturated hydrocarbons influence the tendency of the fuel to form deposits on the nozzle-atomizer needles is indicated by the data of Table 125.

In operation on direct-distillation diesel fuel, we observe small

TABLE 125

Influence of Unsaturated Hydrocarbons on Nozzle-Atomizer Needle Tarring

| 1 Температура, °С | Дизельное топливо термического крекинга. Содержание непредельных — 35% (2) | | Дизельное топливо прямогонное (5) | |
|---|---|---|---|---|
| | усилие извлечения иглы из корпуса распылителя, кг (3) | толщина лаковой пленки на игле, мк (4) | усилие извлечения иглы из корпуса распылителя, кг (3) | толщина лаковой пленки на игле, мк (4) |
| 155 | 12 | 0,75 | 6 Свободна | 7 Нет |
| 170 | 15 | 2,5 | » | 8 Следы |
| 185 | >15 | 3,25 | 3 | 0,5 |

1) Temperature, °C; 2) thermal-cracking diesel fuel. Unsaturated content 35%; 3) effort required to pull needles from atomizer housing, kg; 4) thickness of varnish film on needle, μ; 5) direct-distilled diesel fuel; 6) free; 7) none; traces.

amounts of deposit on the atomizer needles only at 185°, while the needles themselves are touched only at spots. The thermal-cracking component included in the composition of the diesel fuel forms a varnish film 0.75 mm thick at a temperature as low as 155°, and the effort necessary to extract the needles from the atomizer housings rises to 12 kg. With rising temperature, the quantity of deposits on the needles increases, and an effort in excess of 15 kg is required to extract them.

Together with sticking of the nozzle-atomizer needles during operation of diesel engines, we sometimes observe breakdown of the felt inserts in the fine filters. As has been shown by research carried out by G.P. Otkupshchikov, this may be accounted for as follows. Diesel fuels obtained from naphthene-base oils are subject to saponification in some cases as a result of their high content of naphthenic acids. The naphthenic soaps formed as a result are eliminated by subsequent water washing. However, they are not always completely removed, particularly when the washing procedure is inadequate. During the summer period of operations, particularly in the southern regions of the country, the

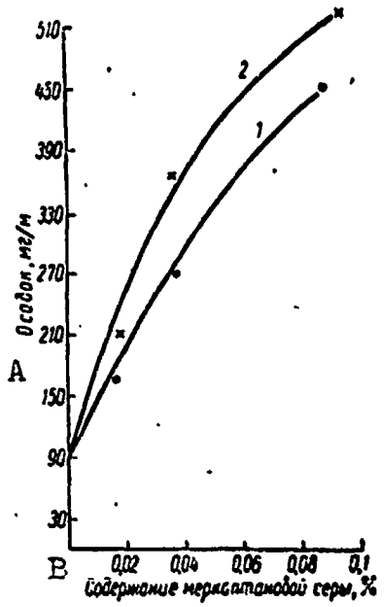


Fig. 163. Influence of aromatic mercaptans on sediment formation in catalytic gas oil [10]. 1) Thiophenol; 2) thiocresols. A) Deposits, in g/m; B) content of mercaptan sulfur, %.

temperature of the fuel passing through the fine-cleaning filter reaches 50 – 70°. If the fuel contains naphthenic soaps, they are readily hydrolyzed in the presence of water at such temperatures to form alkalis. The latter are extremely aggressive toward the felt, so that the felt inserts break up rapidly. In cases where this has happened, the filter glasses always have water with an alkaline reaction at the bottom.

Contamination of diesel fuel by water is further intolerable because, firstly, it causes corrosion of the fuel tanks and fuel apparatus, particularly when high-sulfur diesel fuels are employed, and, secondly, because when the temperature drops below 0° with water present in the fuel, ice crystals form; these are capable of clogging the engine's fuel system.

## PROPERTIES OF FUEL THAT GUARANTEE NORMAL COMBUSTION

The normal combustion of the fuel and the completeness with which it is burned in a diesel are determined basically by the chemical and fractional compositions of the diesel fuel.

Since the fuel burns in the vapor phase, it is necessary that, on its entry into the combustion chamber in a finely atomized liquid state, it have time to undergo complete vaporization during a very short period reckoned in thousands of a second. Depending on the speed of the engine, the time available for evaporation of the fuel varies over a relatively wide range. Consequently, the specifications for vaporizability of diesel fuels – a property characterized by their fractional composition

are different for engines running at different speeds.

Low-speed large stationary diesels have low requirements as to the fractional composition of their fuels and perform quite normally on such heavy fuels as mazout.

On the other hand, fractional composition is an essential factor for the high-speed diesels used in transportation; its importance is determined by the design of the engine's combustion chamber.

Figure 164 shows the influence of fuel fractional composition on the specific fuel consumption and the rate at which the pressure rises in engines that differ in combustion-chamber design. The data presented indicate that in the boiling-temperature range of fuels selected (ranging from kerosene to solar oil), the fractional composition of the fuel has virtually no influence on specific consumption for engines that have antechambers and hot swirl chambers. Engines with swirl chambers that are not heated are more sensitive to fuel fractional composition. As the vaporizability of the fuel ($300^{\circ}$) increases from 10% (solar oil) to 70% (80% kerosene and 20% solar oil), the specific consumption declines by 4.5%. Most sensitive to fuel fractional composition is the single-chamber engine. The use of a fuel 90% of which boils up below $300^{\circ}$ in such an engine instead of a fuel only 30% of which boils up below $300^{\circ}$ makes it possible to lower the specific fuel consumption by 16%.

It is necessary to note that these relationships apply for fuels boiling below $300^{\circ}$. When a fuel that is higher-boiling than solar oil is used in high-speed engines – even in the antechamber types, which are least demanding as regards fractional composition – the performance of the engine already shows considerable deterioration.

Such fuels do not have time for complete vaporization and prompt formation of a mixture of the necessary quality with the air, so that

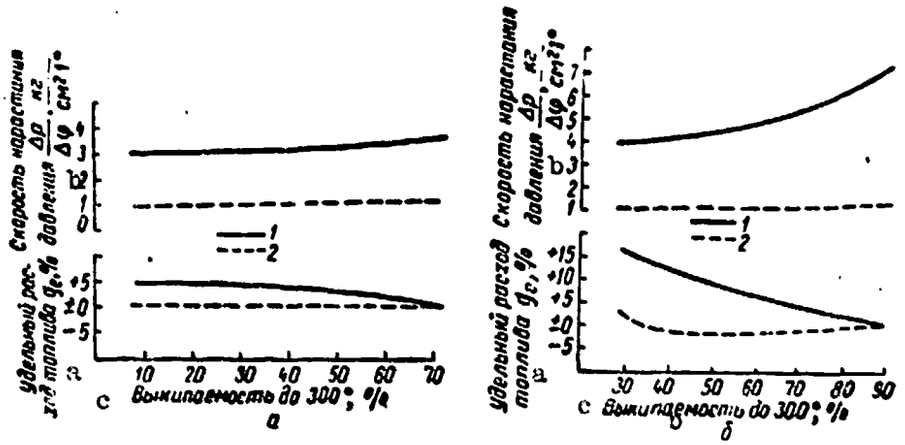


Fig. 164. Influence of fractional composition of fuel on specific fuel consumption and rate of pressure rise in cylinder. a) 1) Engine with swirl chamber; 2) engine with antechamber; b) 1) Engine with single chamber; 2) engine with hot swirl chamber. A) Specific fuel consumption $g_e$, %; B) rate of pressure increase $\Delta p/\Delta\Phi$, kg/cm$^2$ - degree; C) percentage boiled out below 300°.

their combustion is drawn out and completed only during the expansion stroke. That part of the fuel which did not evaporate in time undergoes thermal decomposition as a result of the high temperatures, with formation of carbonaceous substances that are hard to burn. As a result, the temperature of the exhaust gases rises, the heat losses increase, scaling is aggravated, the exhaust becomes smoky, and the economy of the engine diminishes.

Another contributory factor in the poor combustion of excessively heavy fuels is their increased viscosity and the resulting larger size of the atomized fuel drops.

According to the curves of Fig. 164, the rate of the pressure build-up in the engine increases, particularly in a single-chamber engine, when the fractional composition of the diesel fuel is lightened. This is explained as follows: as a result of the fuel's self-ignit[illegible]

lag, the lower-boiling fuel has time to vaporize before self-ignition begins and does so to a considerably greater degree than does a higher-boiling fuel. Consequently, by the time the flame appears, almost all of the light-fraction fuel injected into the engine is participating in combustion. As a result, the rate of pressure build-up is higher and when a certain limit is reached, combustion of the fuel in the engine will be accompanied by knocking.

For fuels that possess large self-ignition lags, i.e., those having low cetane numbers, this limit is reached earlier as the fractional composition is lightened. But when a high-cetane fuel is used, even in antechamber engines, knocking is inevitable when the fractional composition of the fuel is lightened excessively, i.e., the engine begins to run "hard."

For diesel fuels obtained from a given raw material, the self-ignition lag becomes longer as the fuels become lighter (the cetane number drops), i.e., as the fractional composition of the fuel is lightened, one factor – excessively rapid vaporization – is compounded by another factor – the increased self-ignition. Consequently, excessive lightening of diesel-fuel fractional composition is just as undesirable as having it excessively heavy.

As concerns the optimum fractional composition for diesel fuels intended for high-speed diesels, it is obvious that this will depend on the design of the engine's combustion chamber. For antechamber engines and engines with heated swirl chambers, a fuel of wide fractional composition boiling in the range from 160 – 180° to 360 – 400° may be used; the proportions of the individual fractions in such a fuel have no great importance. Use of a diesel fuel having narrow boiling ranges is required for single-chamber engines. As indicated by tests, such fuels must boil out in the range from 200 – 300° [3].

However, completeness of vaporization is not alone sufficient to ensure a normal combustion process. We may select a fuel with the optimum fractional composition, but if its cetane number is very low, i.e., if its self-ignition lag is too long, the engine will operate "hard."

The cetane number of a diesel fuel depends on its chemical composition or, more precisely, on the structure of the hydrocarbons composing it. Straight-chain paraffinic hydrocarbons have the highest cetane numbers. As the straight chain becomes more and more branched, the cetane number of the paraffinic hydrocarbons tends to diminish; here, the closer the side chain is to the end of the molecule, the greater will be the drop in cetane number. The cetane numbers of unsaturated hydrocarbons with open chains are somewhat lower than those of the corresponding paraffins.

The naphthenic hydrocarbons are markedly inferior to paraffinic hydrocarbons as regards cetane number, with this number dropping off noticeably as the number of rings in the molecule of the naphthenic hydrocarbon increases. The poorest hydrocarbons as regards cetane number are the aromatics, and particularly hydrocarbons with condensed rings.

As a rule, if the molecular weights of the hydrocarbons are increased by lengthening the molecular chains of the paraffinic hydrocarbons or the side chains of naphthenic and aromatic hydrocarbons, the cetane number rises. Consequently, the cetane numbers of diesel fuels generally rise (Fig. 165) as their fractional composition becomes heavier.

Although cetane number does characterize the self-ignition lag of the fuel, there is rigorous linear relationship between these parameters, as shown by the curves of Fig. 166, and an increase in the

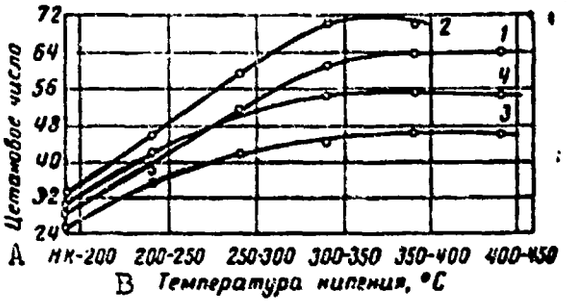


Fig. 165. Influence of diesel-fuel fractional composition on cetane number. 1) Distillate of paraffin-base fuel; 2) refined paraffin-base fuel; 3) distillate of naphthenic-aromatic-base fuel; 4) refined naphthenic-aromatic-base fuel. A) Cetane number; B) boiling point, °C.

fuel's cetane number above 45 – 50 units reduces and, consequently, improves the self-ignition lag of the fuel only slightly.

Apart from the self-ignition lag, the cetane number gives us a basis for inferences concerning other operational properties of a diesel fuel related to the completeness of fuel combustion – namely, the starting properties of the fuel, its tendency to form deposits in the engine, and the nature of the exhaust gases. This is clearly illustrated by the curves of Fig. 167. The starting properties of a diesel fuel may also be observed as a function of cetane number by reference to the time required to start the engine: on a fuel with a cetane number of 53, the engine starts after 3 sec of cranking, while a 38-cetane fuel starts the engine only after 45 – 50 sec of starter operation.

Not only the chemical and fractional composition of the fuel, but also the properties considered above – viscosity, surface tension – and the perfection of the fuel-apparatus design influence the completeness of fuel combustion in high-speed diesel engines.

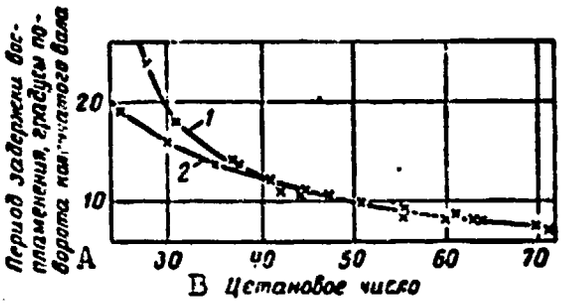


Fig. 166. Relationship between cetane number and self-ignition lag of diesel fuels. 1) Diesel fuel No. 1; 2) diesel fuel No. 2. A) Self-ignition lag, degrees of crankshaft revolution; B) cetane number.

The cetane rating of diesel fuels may be improved either by removing the low-cetane aromatic hydrocarbons from them by one method or another, or by adding special additives that raise the cetane number (see Chapter 14).

GRADES OF DIESEL FUEL

At the present time, the petroleum industry is producing special grades of diesel fuel for high-speed engines running at over 1000 rpm, for medium-speed engines (500 – 1000 rpm) and for slow engines (speeds below 500 rpm). The diesel fuel for the high-speed engines is processed in accordance with GOST 4749-49 and GOST 305-58 (Table 126).

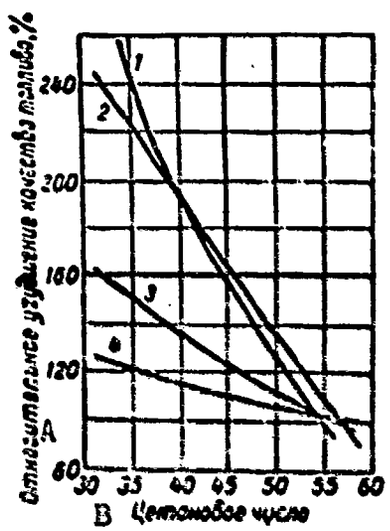


Fig. 167. Influence of cetane number on operational properties of diesel fuels. 1) Starting properties; 2) odor; 3) deposits; 4) smoke. A) Relative deterioration of fuel quality, %; B) cetane number.

The diesel fuel produced after GOST 4749-49 has a low sulfur content and consists of the gas-oil or kerosene-solar petroleum fractions. The DA arctic diesel fuel is intended for high-speed engines operating at ambient temperatures below $-30^{\circ}$. DZ winter diesel fuel is used with air temperatures ranging from zero to $-30^{\circ}$, and the DL summer fuel at fuel temperatures above zero. The special DS diesel fuel is designed for engines that have elevated cetane requirements.

The diesel fuel of GOST 305-58 is refined from high-sulfur petroleums. For this reason, sulfur contents up to 1.0% are tolerated in

TABLE 126

Diesel Fuel for High-Speed Engines

| 1 Показатели | 2 Топливо ГОСТ 4749-49 | | | | 7 Топливо ГОСТ 305-58 | | |
|---|---|---|---|---|---|---|---|
| | 3 ДА | 4 ДЗ | 5 ДЛ | 6 ДС | 8 Л | 9 З | 10 С |
| 11 Цетановое число | 40 | 40 | 45 | 50 | 45 | 43 | 50 |
| 12 Фракционный состав: | | | | | | | |
| 13 10% перегоняется при температуре в °С не ниже | 200 | 200 | — | — | 200 | 170 | — |
| 50% то же 14 | 255 | 275 | 290 | 280 | 295 | 275 | 280 |
| 90% » | 300 | 335 | 350 | — | — | — | — |
| 96% » | 330 | — | — | 340 | 360 | 350 | 360 |
| 15 Вязкость кинематическая, сст: | | | | | | | |
| при 20° | 2,5— | 3,5— | 3,5— | — | 3,0— | 1,8— | 4,5— |
| 16 | 4,0 | 6,0 | 8,0 | | 8,0 | 3,0 | 8,0 |
| при 50° | — | — | — | 2,5— 4,0 | — | — | — |
| 17 Коксуемость 10%-ного остатка в % не более | 0,05* | 0,5 | 0,5 | 0,5 | 0,4 | 0,3 | 0,3 |
| 18 Кислотность в мг KOH на 100 мл топлива не более | 5,0 | 5,0 | 5,0 | 5,0 | 5,0 | 5,0 | 5,0 |
| 19 Зольность в % не более | 0,01 | 0,02 | 0,02 | 0,02 | 0,02 | 0,025 | 0,02 |
| 20 Содержание серы в % не более | 0,2 | 0,2 | 0,2 | 0,2 | 1,0 | 0,6 | 1,0 |
| 21 Проба на медную пластинку | 23 Выдерживает | | | | | | |
| 22 Водорастворимые кислоты и щелочи | 24 Отсутствуют | | | | | | |
| 25 Механические примеси и вода | | | | | | | |
| 26 Температура вспышки в закрытом тигле, °С | 35 | 50 | 60 | 90 | 65 | 45 | 65 |
| 27 Температура застывания в °С не выше | —60 | —45 | —10 | —15 | —10 | —35 | —15 |
| 28 Температура помутнения в °С не выше | — | —35 | —5 | —10 | —5 | —25 | —10 |
| 29 Йодное число, г йода на 100 г топлива | — | — | — | — | 13 | 13 | 13 |
| 30 Содержание фактических смол, мг на 100 мл топлива | — | — | — | — | 100 | 70 | 100 |

*Cokability of fuel.

1) Indicator; 2)fuel after GOST 4749-49; 3) DA; 4) DZ; 5) DL; 6) DS; 7) fuel after GOST 305-58; 8) L; 9) Z; 10) S; 11) cetane number; 12) fractional composition:; 13) 10% distills at temperature (°C) no lower than; 14) same; 15) kinematic viscosity, cst; 16) at: 17) cokability of 10% residue in % no greater than; 18) acidity in mg of KOH per 100 ml [sec] of fuel not above; 19)ash content in % not above; 20) sulfur content in % not above; 21) copper-plate test; 22) water-soluble acids and alkalis; 23) passes; 24) none; 25) mechanical impurities and water; 26) flash point in closed crucible, °C; 27) pour point in °C not above; 28) clouding temperature in °C not above; 29) iodine number, g of iodine per 100 g of fuel; 30) actual-tars content, mg per 100 ml of fuel.

fuel grades L and S and up to 0.6% in grade Z. In view of the fact that high-sulfur oils are basically high-paraffin, distillates of lightened

fractional composition are employed to produce diesel fuels with the required low-temperature properties from these petroleums. Grade Z diesel fuel is produced from the kerosene-gas oil fractions of the petroleum, while the solar fractions are also used to obtain grade L diesel fuel and particularly grade S. Components from catalytic and, at certain plants, thermal cracking are included in grades Z and L diesel fuel. To limit the contents of these components in diesel fuel, two new indices have been introduced into the technical specifications: iodine number and actual-tars content.

To exclude the detrimental effects of the combustion products of sulfur compounds on engine performance when diesel fuels produced after GOST 305-58 are employed, it is necessary simultaneously to employ an oil with the TsIATIM-339 additive or some more effective additive.

Fuel L is employed when the ambient temperature is above zero, and fuel Z at temperatures from zero to $-15^{\circ}$. At lower air temperatures, fuel Z is mixed with tractor kerosene in the following proportions:

| 1 Температура окружающего воздуха, °С | 2 Состав смеси дизельного топлива З и тракторного керосина |
|---|---|
| 3 От −15 до −25 | 4 75% З+25% керосина |
| » −25 » −35 | 50% З+50% » |
| 5 Ниже −35 | 25% З+75% » |

1) Air temperature, °C; 2) composition of mixture of diesel fuel Z and tractor kerosene; 3) from −15 to −25; 4) 75% Z + 25% kerosene; 5) below −35.

The DT-1 fuel may be used as a starting fuel for engines operating on fuels DT-2 and DT-3. Fuel DT-2 is intended for engines with speeds below 300 rpm, and fuel DT-3 for engines with speeds below 200 rpm and horsepowers above 100.

The so-called solar oil produced after GOST 1666-51 (Table 1?)

is used as a fuel for compression-ignition engines operating at 500 – 1000 rpm.

Solar oil is produced by direct distillation of petroleum and represents the fraction with initial boiling at 240 – 260°, 55 – 60% of which boils below 350°. Diesel fuels produced according to GOST 305-58 and 4749-49 may serve as fully adequate substitutes for solar oil.

TABLE 127

Diesel Fuel for Engines Running at Medium and Low Speeds

| 1 Показатели | 2 Соляровое масло (ГОСТ 1666-51) | 3 Моторное топливо (ГОСТ 1667-51) | | |
|---|---|---|---|---|
| | | 4 ДТ-1 | 5 ДТ-2 | 6 ДТ-3 |
| 7 Вязкость кинематическая при 50° в сст не более | 5,0—9,0 | 36,0 | 55,3 | 66,6 |
| 8 До 250° перегоняется в % не более | — | 15 | 15 | 15 |
| 9 Коксуемость, % | — | 3,0 | 3,5 | 4,0 |
| 10 Зольность, % | 0,025 | 0,04 | 0,08 | 0,08 |
| 11 Содержание серы, % | 0,2 | 0,5 | 0,5 | 0,5 |
| 12 Содержание сероводорода, % | 13 Отсутствует | | | |
| 15 Водорастворимые кислоты и щелочи | 14 То же | | | |
| 16 Механические примеси в % не более | 13 Отсутствуют | 0,1 | 0,1 | 0,1 |
| 17 Содержание воды в % не более | 18 Следы | 1,0 | 1,0 | 1,0 |
| 19 Температура вспышки в °С не ниже: | | | | |
| 20 в открытом тигле | 125 | — | — | — |
| 21 в закрытом » | — | 65 | 65 | 65 |
| 22 Температура застывания в °С не выше | —20 | —5 | —5 | +5 |

1) Index; 2) solar oil (GOST 1666-51); 3) motor fuel (GOST 1667-51); 4) DT-1; 5) DT-2; 6) DT-3; 7) kinematic viscosity at 50° in cst not above; 8) percentage distilled below 250°, not above; 9) cokability, %; 10) ash content, %; 11) sulfur content, %; 12) hydrogen sulfide content, %; 13) none; 14) same; 15) water-soluble acids and alkalis; 16) mechanical impurities in %, not above; 17) water content in % not above; 18) traces; 19) flash point in °C not below; 20) in open crucible; 21) in closed crucible; 22) pour point in °C not above.

For low-speed engines with compression ignition, as well as for calorizer engines with low compression ratios, mixed and residual petroleum products processed according to GOST 1667-51 are used as fuels.

Fuel DT-1 is produced by mixing distillates with residual distillation or cracking products; DT-2 and DT-3 are pure residual products

of direct petroleum distillation or cracking of any mixture of residual products with heavy distillates.

Diesel fuel DT-1 is intended for unsupercharged engines with jet atomization, running at speeds from 200 to 500 rpm and developing powers below 400 hp, as well as for other types of engines with speeds from 300 to 500 rpm and powers below 50 hp.

Special devices are required to preheat and clean DT-2 and DT-3 fuels. In view of its high viscosity and pour point, fuel DT-3 is specified for installations equipped with devices for steam preheating of the fuel. The recommended preheating temperature is 35 – 40° for reservoirs, 60 – 65° for sedimentation tanks and filters, and 50 – 60° for the nozzles.

Fuel DT-2 may be used with hot-water heating to a temperature of 45 – 50°.

Apart from the engines listed above, fuel DT-1 may be used in all equipment operating on fuels DT-2 and DT-3 but not having preheater devices.

The foreign specifications for diesel fuel differ little from the standards effective in the USSR. The USA has petroleum-products specifications that include specifications for diesel fuels: the ASTM specifications, Federal specifications, military specifications, and others (Table 128).

The ASTM specifications provide for the production of three grades of fuels for compression-ignition high-speed engines: 1-D, 2-D and 4-D.

The easily vaporized 1-D distillate fuel is a kerosene-ligroin fraction boiling below 330°. This fuel is intended for use in engines operating with variable speeds and loads. As regards its indices, fuel 1-D corresponds to fuel DA (GOST 4749-49).

Distillate fuel 2-D is the petroleum fraction boiling below 385°.

TABLE 128

American Specifications for Diesel Fuels for High-Speed Compression-Ignition Engines

| 1 Показатели | 2 Спецификация ASTM D-975-60T | | | 3 Федеральная спецификация 0-361 | 4 Военная спецификация MIL-E-896 (1950 г.) | | |
|---|---|---|---|---|---|---|---|
| | 1-D | 2-D | 4-D | | 5 1-й класс | 2-й класс | 3-й класс |
| 6 Цетановое число не ниже . . | 40 | 40 | 30 | 40 | 50 | 40 | 35 |
| 7 Фракционный состав, °С: | | | | | | | |
| 8 90% перегоняется . . . . | 288 | 282—357 | — | 357 | 357 | 357 | 315,5 |
| 9 к. к. . . . . | — | — | — | — | 385 | 385 | 385 |
| 10 Вязкость кинематическая при 38°, *сст*: | | | | | | | |
| 11 минимум . . . . . | 1,4 | 2,0 | 5,8 | — | 2,1 | 2,1 | 1,5 |
| 12 максимум . . . . . | 2,5 | 5,8 | 26,4 | 6,0 | 6,0 | 6,0 | 2,3 |
| 13 Коксуемость 10%-ного остатка | 0,15 | 0,35 | — | — | — | — | — |
| 14 Зольность в % не более . . | 0,01 | 0,02 | 0,10 | 0,02 | 0,01 | 0,01 | 0,01 |
| 15 Содержание серы в % не более | 0,5 | 1,0 | 2,0 | 1,25 | 1,00 | 1,25 | 1,00 |
| 16 Содержание воды: | | | | | | | |
| 17 % объемн. не более . . . | 18 Следы | 0,10 | 0,50 | — | — | — | — |
| 19 % вес. » » . . . | — | — | — | 0,01 | 0,03 | 0,05 | 0,03 |
| 20 Температура вспышки в °С не менее . . . . . | 38 | 52 | 54 | 38 | 60 | 60 | 60 |
| 21 Температура застывания, °С | * | * | * | —7 | —18 | —29 | —40 |
| 22 Температура помутнения, °С | — | — | — | —7 | —12 | —23 | —34 |

*The specification provides for establishment of additional indices by agreement with the customer. The pour points are established by agreement with observance of the following condition: lacking preheaters, the pour point must be 5.6° lower than the ambient temperature.

1) Index; 2) ASTM Specification D-975-60T; 3) Federal Specification 0-361; 4) Military Specification MIL-E-896 (1950); 5) class 1: 6) cetane number not below; 7) fractional composition, °C; 8) 90% distilled; 9) end of boiling; 10) kinematic viscosity at 38°, cst; 11) minimum; 12) maximum, 13) cokability of 10% residue; 14) ash content in % not above; 15) sulfur content in % not above: 16) water content; 17) % by volume not above; 18) traces; 19) % by weight; 20) flash point in °C, not below; 21) pour point, °C; 22) cloud point, °C.

This heavier fuel, which is harder to vaporize, is intended for use in industrial and heavy-duty transport engines. Fuel 4-D is intended for engines running at medium speeds and certain types of low-speed engines.

Federal Specification 0-361 provides for production of one grade of diesel fuel, which differs only slightly in its properties from

TABLE 129

Specifications of Other Countries for Diesel Fuels for High-Speed Engines

| 1 Показатели | 2 Англия DEF-2402 | | | 4 ГДР TGL 4938 (1959) | | 5 ФРГ DIN 51601 (1959) |
|---|---|---|---|---|---|---|
| | Температура застывания 3 | | | | | |
| | +20° | 0° | −30° | DKM | DK | |
| 6 Удельный вес $\rho_4^{20}$ | — | — | — | 0,810—0,900 | 0,810—0,880 | 0,820—0,860 |
| 7 Цетановое число не ниже | 47 | 47 | 45 | 40 | 40 | 40—45 |
| 8 Фракционный состав, °С: | | | | | | |
| a а) 80% выкипает | — | — | — | 360 | — | — |
| b б) 90% » | 357 | 357 | 316 | — | 360 | 360 |
| c в) к. к. | 385 | 385 | 343 | — | — | — |
| 9 Вязкость кинематическая, сст: | | | 10 | | | |
| при 20° | 1,8—7,5 | 1,8—7,5 | Не ниже 1,4 | 3,0—9,4 | 3,0—9,4 | 1,8—10,0 |
| 11 при 38° | 0,20 | 0,20 | 0,14 | — | — | — |
| 12 Коксуемость 10%-ного остатка не более | 0,5 | 0,5 | 0,5 | — | — | — |
| 13 Коксуемость всего продукта не более | — | — | — | 0,1 | 0,1 | 0,1 |
| 14 Содержание твердого асфальта не более | — | — | — | 0,2 | — | — |
| 15 Зольность в % не более | 0,01 | 0,01 | 0,01 | 0,02 | 0,01 | 0,02 |
| 16 Содержание серы в % не более | 1,0 | 1,0 | 1,0 | 1,5 | 0,5 | 1,0 |
| 17 Проба на медную пластинку | 18 Выдерживает | | | — | — | — |
| 19 Содержание воды в % не более | 0,05 | 0,05 | 0,05 | 0,3 | 0,1 | 0,1 |
| 20 Содержание механических примесей в % не более | 0,01 | 0,01 | 0,01 | 21 Отсутствуют | | 21 Отсутствуют |
| 22 Температура вспышки °С не менее | 66 | 66 | 38 | 55 | 55 | — |
| 23 Температура застывания в °С не выше | −7 | −18 | −34 | 24 Летом 0 зимой −10 | 0 −15 | — |
| 25 Температура начала выделения парафинов в °С не выше зимой | — | — | — | −5 | −10 | — |
| 26 Фильтруемость по Хагемашу и Химмерингу в °С не выше | — | — | — | — | — | 27 Летом до 0, зимой до −1 |
| 28 Коррозия цинковой пластинки (потеря веса) в мг не более | — | — | — | — | 4 | 4 |

1) Index; 2) England: DEF-2402; 3) pour point; 4) German Democratic Republic, TGL 4938 (1959); 5) Federal Republic of Germany, DIN 51601 (1959); 6) specific gravity $\rho_4^{20}$; 7) cetane number not below; 8) fractional composition, °C; 8a) 80% boils out; 8c) end of boiling; 9) kinematic viscosity, cst; 10) not below; 11) at; 12) cokability of 10% residue not above; 13) cokability of entire product not above; 14) solid-asphalt content not above; 15) ash content in % not above; 16) sulfur content in % not above; 17) copper-plate test; 18) passes; 19) water content in % not above; 20) content of mechanical

impurities in % not above; 21) none; 22) flash point, °C not below; 23) pour point in °C not above; 24) summer 0, winter -10; 25) temperature at which paraffins begin to separate, °C, not above (winter); 26) Hagemasch-Himmering filterability °C, not above; 27) summer to 0, winter to -12; 28) zinc-plate corrosion (weight loss) in mg not above.

grade 2-D. Both of these grades correspond approximately to fuel L, which is produced according to GOST 305-58.

The Military Specification was introduced in the USA in 1950 to supersede Navy Specification 7-0-2-e and Army Specification 2-102-c.

The Military Specification embraces three classes of fuels. Class 1 is intended for submarine engines and for other special-purpose engines operating at ambient-air temperatures above -12°; class 2 is a summer diesel fuel for automotive and tank engines; class 3 is a winter diesel fuel.

In examining the military specification our attention is drawn to the high admissible content for all of the diesel fuels and the low cetane ratings of the summer and winter grades.

Table 129 presents British, East German and West German specifications for diesel fuels for high-speed engines. Diesel fuels of three grades are used in England; these have cetane ratings of 45 - 47 and pour points of -7, -18 and - 34°. Sulfur contents in these fuels may run up to 1%.

Two grades of diesel fuels are produced in the German Democratic Republic: type DKM, which is used in engines having piston speeds below 7 m/sec, and DK, which is used in engines with piston speeds above 7 m/sec. The Federal Republic of Germany produces only one grade of diesel fuel. The density ranges are standardized for all grades of diesel fuel; here, if the fuel's density lies outside the specified limits, provision is made in West Germany for adjusting the fuel apparatus.

In contrast to the specifications of other countries, the corrosive properties of the diesel fuels produced in both East and West Germany are evaluated not indirectly – by acid number – but directly, from the weight loss of a zinc plate. The low-temperature properties of diesel fuels are determined in West Germany in a filtering apparatus, rather than from the cloud and pour temperatures. This method gives a more correct evaluation of the fuel's behavior at low temperatures. In both West and East Germany, addition of kerosene to diesel fuel or heavy gasoline is permitted when the air temperature drops below $-14^{\circ}$, although the East German specifications make it a condition that the viscosity of the fuel not drop below 3.0 cst when this is done, nor its flash point below $55^{\circ}$. The West German specifications restrict not only the lower limit, but also the upper limit of cetane rating.

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Chapter 19

# BOILER FUELS

## GENERAL REMARKS

During the first 50 years of the existence of steam power installations, the steam boilers were stoked exclusively with coal and woods. With the development of the petroleum industry, the question of using petroleum and its refinery products as fuels became acute, since liquid fuel (mazout) produces 1.5 times as much heat as coal and 3 times as much as wood.

The use of liquid fuel was delayed by the lack of effective methods of burning it. Attempts to burn liquid fuel in the fireboxes in the form of fine sprays or droplets or by pouring it over a tray having a broad surface produced no results. Combustion was accompanied by loud noise, the fuel did not burn completely, and the firebox did not reach the required temperature.

An effective method for burning liquid fuel in atomized form was proposed by A.I. Shpakovskiy (1865) and D.I. Mendeleyev (1867). This method came into practical application in 1880, when V.G. Shukhov built a special nozzle for combustion of fuel; in this nozzle, the petroleum fuel, which came out through a narrow passage, is converted into a fine spray by steam force. Entering the firebox, the atomized fuel vaporizes, is thoroughly mixed with air, and burns to completion. Steam atomization proved so effective that it is still being used successfully to this day.

In the middle eighteen-nineties, the Tentelevsk chemical plant

at St. Petersburg developed a system for mazout firing of steam boilers using mechanical nozzles in which the fuel is atomized by the pressure set up by a pump. The mechanical nozzles eliminate the large consumption of steam, which is of great importance for seagoing vessels, since the fresh-water requirement is reduced. The introduction of nozzles for combustion of liquid boiler fuel made it possible to create new types of boiler installations with high steam output, high thermal loads on the heating surface, and high efficiencies. Liquid boiler fuels came into widespread use in all branches of the national economy; this is accounted for by the great advantages of liquid fuels over fuels of other types.

These advantages include:

– a high heat of combustion, which makes it possible to burn liquid fuels at high firebox stresses, which may reach 1,500,000 kcal/$m^3$·hour as against 350,000 kcal/$cm^3$·hour with solid fuels;

– the possibility of reaching high completeness of combustion with relatively low excess-air ratios;

– convenience in supplying the fuel to the firebox and the possibility of automating this process;

– the simplicity of transportation, loading and unloading of the fuel at the points of production and consumption and ease of storage;

– the precision and simplicity with which the thermal regime of the installations can be regulated.

Special requirements are set forth for marine-boiler fuels; they must make it possible to operate the installation under various climatic conditions without cumbersome accessory devices (preheaters, settling tanks, and so forth), contain the smallest possible quantity of ballast, i.e., unnecessary impurities (ash, moisture), have high heats of combustion, occupy a small volume per unit weight, and burn

well (if possible, without smoke) in marine-boiler fireboxes that are simple in design and small in dimensions.

The heat balance of a boiler installation, which determines the influx and expenditure of heat, is its performance index. The expenditure side of the balance includes all productive expenditure going for the performance of work and unproductive expenditure, which is composed of the various heat losses. If the heat introduced into the firebox (which is equal to the heat of combustion of the fuel in question) is taken as 100, the productive and unproductive consumptions observed with a liquid fuel are distributed approximately as shown in Fig. 168.

The unproductive losses are by no means a constant quantity. Heat losses can and should be reduced by efficient utilization of the heat wastes, selection of an efficient combustion mode, improving the heat insulation of the boiler installation, and so forth.

To raise the operating efficiency of the installation, it is necessary to observe exactly the operating procedure for the boiler and to maintain the heating surface in proper order at all times. Practical experience has shown, for example, that cleaning the heating surface and maintaining it in the proper condition is alone sufficient to increase the productivity of the installation by 10% or more. Air blown by ventilators is fed into the ash pit of the firebox to support combustion.

Completeness of combustion is achieved by thorough mixing of the fuel particles with air. Consequently, the smaller the fuel particles composing the fuel-air mixture, the more complete will be the combustion process.

A necessary condition for normal operation of a boiler installation is completeness of fuel combustion with the smallest practically feasible air excess.

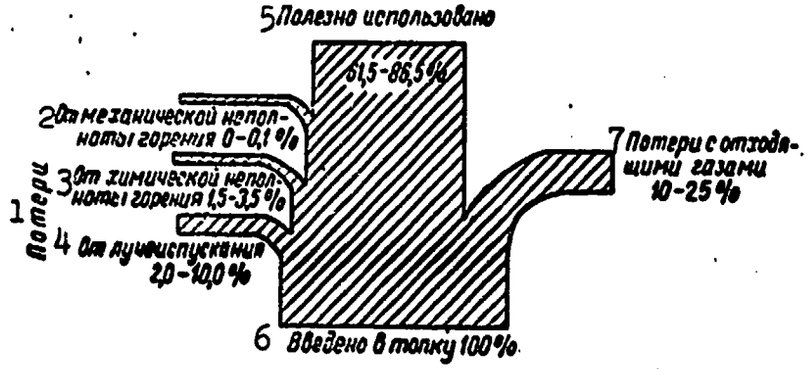


Fig. 168. Heat balance of boiler installation. 1) Losses; 2) from mechanical incompleteness of combustion 0-0.1% 3) from chemical incompleteness of combustion 1.5-3.5%; 4) due to radiation 2.0-10.0%; 5) utilized; 6) introduced into firebox 100%; 7) losses with exhaust gases 10-25%.

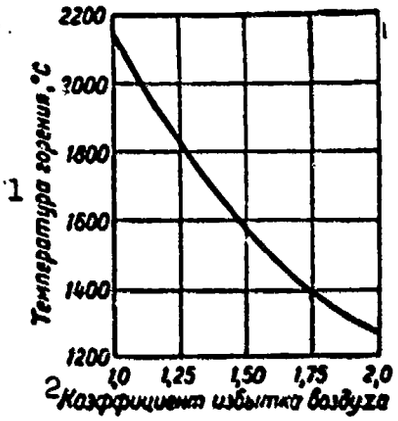


Fig. 169. Curve showing combustion temperature of fuel-air mixture as a function of excess-air ratio. 1) Combustion temperature, °C; 2) excess-air ratio.

The combustion temperature of the fuel-air mixture varies as a function of excess air. The relationship between these parameters is shown in Fig. 169, where the fuel is mazout with an actual water content of 0.3% and a $VU_{50}$ viscosity of 6 with mechanical atomization.

To a major degree, the completeness of combustion of mazouts depends on their quality. Heavy mazouts, and cracking mazouts in particular, which contain up to 14-16% of asphaltenes, carbenes and carboids, do not burn completely and produce deposits on the tube surfaces. The smaller the tendency of the fuel to produce products of incomplete combustion, the more economically and reliably will the installation perform. Various additives are introduced into mazouts abroad to ensure completeness of combustion. According to N.A. Butkov, one such additive – Pyrolin – consists almost entirely of aromatic hydrocarbons

with the low crystallization temperature of naphthalene homologs. It is assumed that the most complete combustion of mazouts with Pyrolin added is achieved by reducing the tendency of resinous alphalt and higher aromatic compounds in the mazout to polymerization and condensation reactions.

A number of other additives are also known; these are produced under the trade names Dislip F, Fuelslip, Nalco, and so forth. The additive ekstsit [sic; Excite? X-ite?], which, according to the VTI, consists basically of 70% NaCl and 20% $(NH_4)_2SO_4$ [3], is used in the USA.

The domestic additive Ekoton has the following composition: 1.5% of elementary sulfur, 79.5% NaCl, 5% $(NH_4)2SO_4$, 6.5% $Al(OH)_3$, 3% ZnO, 3% CuO, 1.0% $FeSO_4$ and 0.5% $H_2O$ [3].

In 1957, under the supervision of N.A. Butkov, the Soviet additive vnii np-102 was developed to permit more efficient combustion of high-viscosity sulfur-containing mazouts. Tests of the additive conducted during 1958 by naval vessels confirmed its effectiveness. It was established that the additive improves the combustion process, reduces heat losses due to chemical incompleteness of combustion, and reduces nozzle cokability and the amount of soot and scale formed on the heating surfaces to a considerable degree.

Liquid boiler fuel, which represents the heavy petroleum residues of refining (direct distillation and cracking) together with products of thermal refining of coals and fuel shales, is used for combustion in marine fireboxes, the fireboxes of stationary boiler installations, and for technical purposes (in steel smelting and in thermal, heating and other industrial furnaces). At times, raw heavy petroleums that are deficient in the light fractions are used as boiler fuels.

No single approved classification has been established for liquid

boiler fuels. The liquid boiler fuels produced by the industry may be classified on the basis of origin, sulfur content, and field of application. In accordance with their origin, boiler fuels are classified as follows:

1) petroleum boiler fuels, which are residual products of petroleum refining (direct distillation and cracking) or raw petroleums that cannot be used for refining for a variety of reasons;

2) coal fuels – residual products from the distillation of tars obtained in semicoking of coals;

3) shale fuels – neutralized shale tars (shale oil) produced in semicoking of shales in internally heated furnaces.

Mazouts are classified as follows on the basis of sulfur content:

1) low-sulfur mazouts, containing no more than 0.5% sulfur;

2) sulfur-containing mazcuts – sulfur content not above 1%;

3) high-sulfur mazouts, containing up to 3.5% of sulfur.

On the basis of field of application, liquid boiler fuels are classified as follows:

1) fleet mazout – of petroleum origin, with properties elevated for vessels and ships of the navy and fishing fleet;

2) fuel mazout (petroleum fuel, heavy petroleums, shale and coal mazouts), which is used for stationary boilers, industrial furnaces, and ships of the navy and fishing fleet.

As regards composition and the type of raw material, fuel mazouts are classified as low-paraffin and paraffin-containing. Further, straight-run mazouts and cracking mazouts are distinguished, the latter being a residue of the cracking process.

BASIC PROPERTIES OF LIQUID BOILER FUELS

The specifications laid down for the quality of boiler fuels are determined by a number of physicochemical indices: heat of combustion,

viscosity, flash and pour points, content of mechanical impurities, ash, sulfur, water, and gummy substances. These boiler-fuel quality indices characterize their operational properties and make it possible to select the field and conditions for application of the various fuel grades.

Heat of Combustion

One of the basic factors that enable us to judge the quality of a fuel is its heat of combustion. This determines the possibility of increasing the thermal stress in the firebox volume and the specific fuel consumption.

For fuels used on seagoing vessels, the heat of combustion is of particularly great importance, since it makes it possible to increase the sailing range with a given weight of fuel taken into the bunkers.

At the present time, heat-of-combustion specifications are included in the GOST technical specifications; for fleet mazouts, nonconformity of the combustion-heat specifications to the technical specifications constitutes one reason for rejection.

The heats of combustion of fuels depend on their elementary composition, which is different for different fuel grades. A high heat of combustion is ensured in liquid fuels by a high H:C ratio in them and a low ash content.

The oxygen, nitrogen and sulfur that are included in the elementary composition of a fuel reduce the fuel's heat of combustion, as do the moisture W and the noncombustible mineral substances (ash) A present in it, the latter representing the fuel's ballast.

In thermal-engineering calculations and evaluation of boiler fuels, they are characterized by:

a) the working mass of the fuel, which indicates what fuel is being fed into the firebox:

$$C^p + H^p + O^p + N^p + S_n^p + A^p + W^p = 100\%;$$

b) the dry (dehydrated) mass of the fuel:

$$C^p + H^p + O^p + N^p + S_n^p + A^c = 100\%;$$

c) the combustible mass of the fuel, which represents the water- and ash-free composition of the fuel:

$$C^r + H^r + O^r + N^r + S_n^r = 100\%.$$

In these formulas, the superscripts r, s and g denote the working, dry and combustible masses of the fuel, while $S_l$ is the volatile combustible sulfur. Thermal calculations for boilers are normally based on the working mass of the fuel.

TABLE 130

Elementary Composition of Various Grades of Mazout

| Продукт 1 | $W_l^p$, % | $A_l^p$, % | $C_l^p$, % | $H_l^p$, % | $S_n^p$, % | (O+N), % |
|---|---|---|---|---|---|---|
| Мазут флотский 12 . . 2. . . . | 0,94 | 0,03 | 84,68 | 12,05 | 0,71 | 1,59 |
| Мазут сернистый 12 . . 3. . . . | 0,16 | 0,03 | 85,74 | 11,10 | 2,05 | 0,92 |
| Мазут сернистый топочный 20 4. | 0,00 | 0,03 | 84,87 | 11,18 | 2,11 | 1,81 |
| Мазут сернистый топочный 40 5. | 0,00 | 0,02 | 85,15 | 10,75 | 2,00 | 2,08 |
| Ярегская нефть . 6. . . . . | 0,99 | 0,03 | 85,20 | 11,58 | 1,16 | 0,98 |

1) Product; 2) fleet mazout 12; 3) sulfur mazout 12; 4) firebox sulfur mazout 20; 5) firebox sulfur mazout 40; 6) Yarega petroleum.

The elementary composition of boiler fuels undergoes considerable change as a result of deeper-reaching refining processes and the use of sulfur-containing raw materials. The higher the viscosity and specific gravity of a mazout, the higher will be the carbon content in it and the lower its hydrogen content. Moreover, the contents of sulfur, oxygen and nitrogen are elevated in the more viscous mazouts. Viscous cracking mazouts contain from 87.0 to 88.5% carbon and from 10.5 to 11.5% hydrogen. Low-viscosity mazouts accordingly contain from 83.5 to 85.5% of carbon and from 11.4 to 12.2% of hydrogen. The sul-

fur content in viscous cracking mazouts from nonsulfurous petroleums may reach 1%, and 3.5% in sulfurous mazouts (Table 130).

Knowing the elementary composition of a fuel, we may determine its heat of combustion from empirical formulas. The most widely used formula among us is that of D.I. Mendeleyev (page 198, Chapter 7).

The heat of combustion is determined with greater accuracy by experiment, using a bomb calorimeter (see Chapter 3). The heat of combustion of the combustible mass of viscous cracking mazouts is lower than that of straight-run mazouts by 2-3.5%. The difference between the heats of combustion of sulfurous and low-sulfur mazouts of the same grades is as high as 2%.

As the specific gravity of liquid fuel changes, its heat of combustion also changes. The heavier the fuel, the smaller will be its unit-weight heat of combustion. According to GOST specifications, the heat of combustion of fleet mazouts must be no lower than 9870 kcal/kg. The heat of combustion of firebox mazouts depends on their grade and the raw material from which they were produced. The lowest heat of combustion, 9450 kcal/kg, has been set for mazout 200, which comes from high-sulfur raw material.

Apart from the unit-weight heat of combustion, the heat of combustion computed for unit volume is also of considerable interest to the operations engineer; it is determined by the formula

$$K_p^p = Q_n^p d_4^{20} \text{ kcal/liter}$$

The unit-volume heat of combustion of cracking mazouts is normally higher than that of straight-run mazouts.

For purposes of comparison, and for resolving questions that arise when one grade of fuel is to be replaced by another, as well as for establishment of fuel-consumption norms and planning fuel requirements, a conventional unit of heat of combustion equal to 7000 kcal/kg

has been introduced.

A fuel with a working-mass heat of combustion of 7000 kcal/kg is known as conventional fuel.

The qualities of fuels are compared on the basis of the fuel calorific equivalent, which is determined by the formula

$$\vartheta_{кал} = \frac{Q_н^р}{Q_{усл}^р} = \frac{Q_н^р}{7000}.$$

The calorific equivalent is ~1.4 for mazout.

The necessary consumption of a liquid boiler fuel can be established proceeding from the total useful expenditure of heat, the heat of combustion, and the efficiency of the boiler or furnace:

$$B = \frac{Q_{пол}}{Q_н \eta},$$

where B is the fuel comsumption in kg, $Q_{pol}$ is the useful heat expenditure, $Q_n$ is the lower-limit heat of combustion of the fuel, and $\eta$ is the efficiency of the boiler or furnace.

Viscosity of Liquid Boiler Fuels

Like heat of combustion, viscosity is a basic technical property of mazouts that determines the possibility and conditions of using them.

The viscosity of mazouts has been adopted as a basic index for grading them. It is measured with a standard viscosimeter and the viscosity value is given in VU degrees. The viscosity of boiler fuels is determined for different temperatures: for fleet-grade FS-5 and F-12 mazouts at 50°, for F-20 at 75°, and for petroleum fuel (mazout) at 80°, except for mazout 200, whose viscosity is determined at 100°. The viscosity values found for the mazouts at these temperatures do not enable us to form judgments as to their viscosity-temperature characteristics.

At the same time, the difficulties that arise in conducting

operations involving the use of mazouts, such as shipping, transfer from railroad tank cars, tankers and barges, pumping through storage-dump lines and pipelines in ships, are governed by the viscosity properties of the mazouts to a greater extent than by the pour point.

Figure 170 shows curves of the viscosity of mazouts as a function of temperature in the range of above-zero temperatures. It can be seen that in the region of high temperatures – from approximately 50° on up – the curves for mazouts of various grades are shallow and the viscosities vary only slightly as a function of temperature. As a rule, the absolute viscosity figures will be the larger the heavier the fuel and the higher its gum content. At temperatures of the order of 90-100°, the viscosities of various grades of mazout are closely similar.

For normal combustion of liquid boiler fuels using nozzles, and to ensure uniform feed of fuel to them, the viscosities of fuels should not exceed a certain limit. This requirement is connected with the influence of viscosity on the fineness and uniformity of fuel atomization.

It will be seen from Fig. 171 that the higher the viscosity, the greater will be the average diameter of the droplet. Deterioration of atomization fineness brings with it a rise in smokiness of the exhaust due to incomplete combustion and increased fuel consumption. Specific mazout viscosities are required for the various types of nozzles and maintained by heating the fuels in the oil preheaters.

The preheating temperature selected depends on the grade of fuel.

The required limiting viscosities for the various grades of mazouts and their preheating temperatures are listed by A.I. Dvoretskiy [5] as functions of nozzle type. According to the data given, mazout viscosities no higher than 15° VU are recommended for steam nozzles

and no higher than 6° VU for mechanical nozzles; here, the preheating temperature of the mazouts varies from 45° to 100°, depending on grade. For boiler installations with elevated parameters, steam-nozzle mazout viscosities of about 7° VU are recommended; for mechanical nozzles, the figure is about 4° VU.

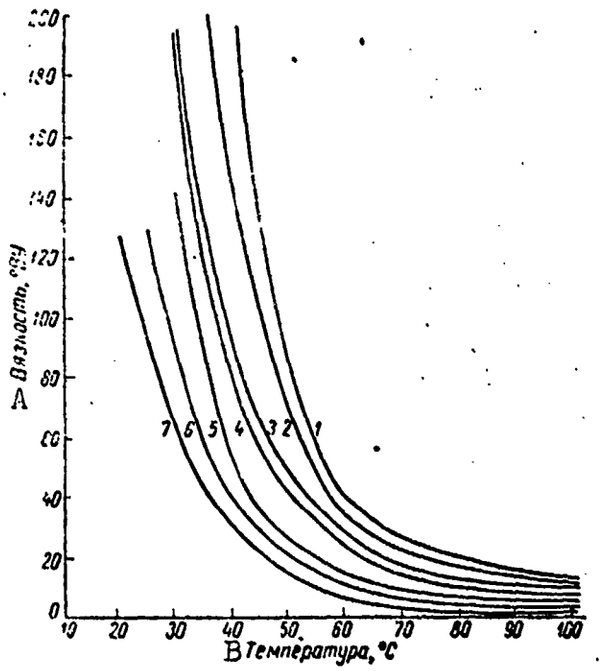


Fig. 170. Curves showing boiler-fuel viscosities as functions of temperature. 1, 2, 3, 4) Grade 80, 60, 40 and 20 firebox mazouts; 5) Yarega petroleum; 6) shale mazout; 7) fleet mazout 12. A) Viscosity, degrees VU; B) temperature, degrees C.

The viscosity of the mazouts is usually even lower for mechanical nozzles used in the boiler installations of seagoing vessels than for stationary installations, and does not exceed 2-3° VU; to ensure this viscosity, fleet mazouts are heated as follows: FS-5 to 65-75°, F-12 and F-20 to 100°. The preheating temperature of the mazout is easily found from the mazout-viscosity nomogram [6] if the grade of mazout and the necessary viscosity for the nozzle are known.

Normal operation of boiler installations is ensured, even on

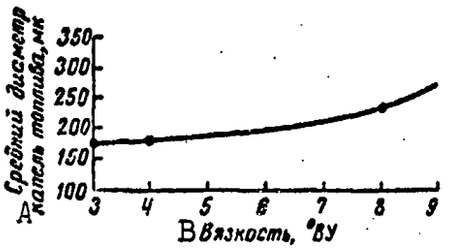


Fig. 171. Influence of viscosity on average droplet diameter in atomization. A) Average fuel-droplet diameter, μ; B) viscosity, °VU.

heavy cracking residues, semiasphalts and petroleum asphalts, i.e., on fuels having viscosities 5-10 times higher at 80° than those of ordinary commercial mazouts [7, 8], by preliminary heating of the fuel to obtain the required viscosity.

In the region of depressed temperatures from +50° down (see Fig. 170), the viscosities of the various mazouts vary differently, and even minor temperature variations may produce a sharp change in the slope of the viscosity curve. At these temperatures, the viscosities of mazouts depend on many factors: the quality of the raw material, the production method, the depth from which fuel is taken, and the paraffin and gum contents. Under these conditions, the absolute viscosity values and the nature of the viscosity are of importance in evaluating the mobility of the mazouts.

Straight-run mazouts, nonparaffinic types derived from low-sulfur raw material, have a shallow viscosity-temperature curve to 0°, and the viscosity does not rise particularly sharply even at temperatures below 0°. Since they have a low pour point, shipping and transfer are relatively simple at temperatures around 0°.

The viscosity of nonparaffinic cracking mazouts increases more rapidly with falling temperature than that of straight-run mazouts. At the same time, despite the rather high viscosities, cracking mazouts do not relinquish their mobility even at temperatures near the pour point. In this case, the viscosity increases due to thickening, i.e., due to the increase in the viscosity of the noncrystallizing hydrocarbons of the fuel, which make up the major part of its

hydrocarbon component.

Cracking mazouts can be transferred without any special preheating even at temperatures near the pour point, when a pump is used, and can be drained from railroad tank cars with only slight preheating.

Unlike the types discussed above, it is characteristic for paraffinic mazouts that together with the increase in viscosity with diminishing temperature, the ultimate shear stress increases sharply. According to G.I. Fuks, a static shear stress appears at about 20° in a paraffinic mazout, while it is not registered even at 0° in a cracking mazout.

In this case, we observe solidification of the product – the result of crystallization of the high-melting, chiefly paraffinic hydrocarbons present in it, which create a crystalline skeleton (structure) that renders the liquid phase immobile or mobile only with difficulty. Consequently, drainage and pump transfers of paraffinic mazouts at low temperatures require preheating above the pour point.

Pipeline transport of high-viscosity and paraffinic mazouts, particularly in cases of long pipelines, is possible only with continuous pumping at a rate no lower than 1-1.5 m/sec. When pumping ceases, it is necessary to take measures to maintain the temperature of the mazout in the pipeline or to empty the pipeline (by incline drainage, air blowout, pumping a lighter fuel through or by use of a suction pump).

Mazouts produced in refining of sulfur-containing petroleums contain considerable quantities of paraffins and gummy asphaltic substances (Table 131), with the result that as the temperature falls, they not only show increased viscosity, but also lose their mobility (fluidity), usually at temperatures higher than the pour point as determined by the standard method. In this case, the viscosities change

TABLE 131

Viscosity-Temperature Characterization of Mazouts at Low Temperatures

| 1 № образца | 2 Мазуты | 3 Парафины, определенные | | 6 Смолы, % | 7 Асфальтены, % | 8 Вязкость (в °ВУ) при температуре, °С | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 4 методом Залозецкого—Голанда, % | 5 адсорбцией на угле, % | | | 50 | 20 | 10 | | 0 | | —10 | |
| | | | | | | | | 9 макс. | 10 мин. | макс. | мин. | макс. | мин. |
| 1 | 11 Малосернистый мазут Ф-12 прямой гонки | 1,02 | 5,08 | 11,06 | 0,14 | 11,4 | 95,3 | 366 | 267 | 1 000 | 728 | 4 564 | 2 920 |
| 2 | 12 Сернистый крекинг-мазут 12 | 2,54 | 13,10 | 9,47 | 4,28 | 12 | 147,2 | 3 668 | 903 | 17 736 | 3 274 | 52 382 | 10 138 |
| 3 | 13 Сернистый мазут ФС-5 прямой гонки | 1,0 | 7,0 | 9,8 | 0,94 | 4,48 | 33,4 | 468 | 169 | 3 528 | 551 | 21 132 | 2 567 |

1) Specimen No.; 2) mazout; 3) paraffins, determined by; 4) Zalozetskiy-Goland method, %; 5) adsorption on carbon, %; 6) tars, %; 7) asphaltines, %; 8) viscosity (in °VU) at temperature of (°C); 9) maximum; 10) minimum; 11) straight-run low-sulfur F-12 mazout; 12) sulfur-containing cracking mazout 12; 13) straight-run FS-5 sulfur mazout.

as a result of thickening and solidification.

At temperatures from 10° down, the viscosities of sulfur-containing mazouts are much higher than those of nonsulfurous mazouts. At these temperatures, the nature of viscosity is also of importance for sulfurous mazouts. Table 2 presents data given by the author of [9] that characterize the presence and magnitude of two viscosity values for low-sulfur and sulfurous mazouts – the structural and residual viscosities (which correspond to the undisturbed maximum and disturbed minimum structures).

At temperatures of 10° and below, the appearance of structural viscosity is noted in all of the mazout specimens investigated. In

low-sulfur straight-run mazout (specimen 1), signs of structure formation are also detected, although the ratio of maximum to minimum viscosity does not exceed 1.4-1.6 and the numerical values of the structural and residual viscosity are of the same order.

In sulfurous straight-run and cracking mazouts, structure formation is particularly strongly manifested (Fig. 172). For these products, the above ratio reaches 5-7 even at $0^{\circ}$, while at $-10^{\circ}$ it is even larger. The absolute viscosity values of straight-run sulfurous mazout at low temperatures are considerably lower than the viscosities of cracking mazout, but exceed those for low-sulfur mazout.

The viscosity increase associated with the formation of structure is quite detrimental to the pumpability of the mazouts at low temperatures. The results of measurements conducted on a laboratory pumping apparatus may give some idea of the influence of a mazout's viscosity properties on its pumpability. The curves shown on the diagram (Fig. 173) correspond to the mazouts whose viscosity properties are listed in Table 131. It can be seen that at a temperature below $20^{\circ}$, the pumpability of the sulfurous cracking mazout (curve 3) is smaller by a factor of 2.0-2.5 than that of a mazout (curve 1) whose viscosity at $50^{\circ}$ is the same. The pumpability of the low-viscosity sulfurous mazout (curve 2) is also found to be lower at temperatures below $10^{\circ}$ than that of the mazout of curve 1.

When mazouts are used on seagoing vessels, the fuel in some of the tanks assumes the temperature of the outboard water ($10-15^{\circ}$ in summer and below $0^{\circ}$ in winter).

Local preheating is applied on seagoing vessels to reduce viscosity at these temperatures. Here, the mazout is heated only in the region of the pump's intake tube in the tank, and the great mass of the mazout arrives at the pickup without preheating. The limited di-

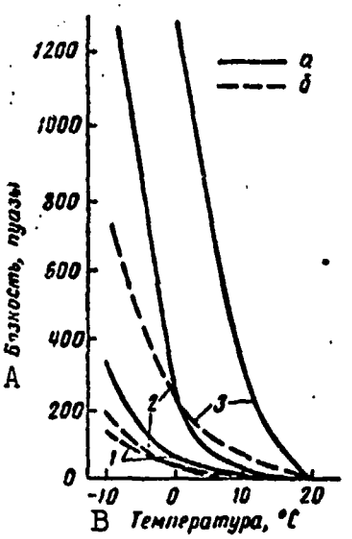


Fig. 172. Viscosity curves of low-sulfur and sulfurous mazouts at low temperatures. 1) Fleet mazout F-12, straight run, $VU_{50}$ = = 12 (from low-sulfur petroleums); 2) fleet mazout, straight run, $VU_{50}$ = 4.38 (from sulfurous petroleum), $\eta_{maks}$ = 1465 (–10); 3) cracking mazout, $VU_{50}$ = = 12 (from sulfurous petroleum), $\eta_{maks}$ = = 3813 (–10); a) viscosity with undisturbed structure; b) viscosity with disturbed structure. A) Viscosity, poises; B) temperature, °C.

mensions of small-boat fuel tanks and the impossibility of installing high-capacity preheating devices in them make it necessary to set forth high specifications as regards the viscosity properties of the boiler fuels for seagoing vessels at temperatures below 20°.

At the present time, the viscosity of FS-5 sulfurous mazout is specified by the GOST regulations not only for 50°, but also for temperatures of 10° and 0°. The viscosity values established here correspond to the viscosities of straight-run F-12 low-sulfur mazout as obtained at the same temperatures.

When boiler fuels are produced at the refineries, and during loading, unloading and shipping operations, they undergo repeated cooling and heating, and this may affect their viscosity-temperature characteristics. According to N.I. Chernozhukov, N.M. Guttsayt, and K.I. Ivanov and other sources, the viscosities of cracking mazouts and paraffinic straight-run mazouts are not constant and depend on prior heat treatment and the degree to which structure has been disturbed.

**Experiments to determine the influence of heat treatment** (at temperatures from +20 to +150°) on the viscosity properties of sulfurous mazouts have shown that the viscosities of mazouts vary differently as functions of prior heating temperature. The viscosities

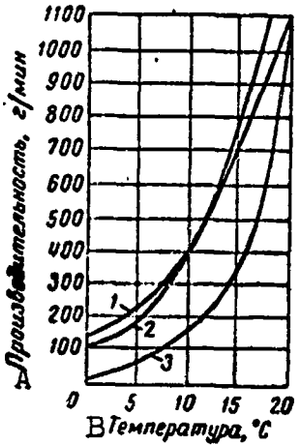


Fig. 173. Pumpability of mazouts as a function of temperature, as determined on laboratory apparatus. 1) Straight-run F-12 mazout ($VU_{50}$ = 11.4); 2) straight-run sulfurous FS-5 mazout ($VU_{50}$ = 4.48); 3) F-12 sulfurous cracking mazout ($VU_{50}$ = 12). A) output, g/min; B) temperature, °C.

vary most sharply with heating temperatures from 70 to 100°; further increases in the heat-treatment temperature above 100° show no noticeable influence on the viscosity variation. **Preliminary heat treatment lowers the** temperature at which a distinctly manifest structure appears in the mazout by almost 20° [9].

The influence of heat treatment on the viscosity of a sulfurous cracking mazout at a temperature of 100° for 30 minutes is shown in Table 132.

It will be seen from Table 132 that preliminary heat treatment reduces the viscosity of the mazout sharply in the initial period. The viscosity drop is associated primarily with melting of solid paraffins and ceresin,

TABLE 132

Influence of Heat Treatment on Viscosity Properties of Cracking Mazout With $VU_{50}$ = 11.84

| 1 Образец | 2 Вязкость (в °ВУ) при | | | |
|---|---|---|---|---|
| | 20° | 10° | 0° | −10° |
| 3 До термообработки | 147,0 | 14 382 | 25 133 | 131 000 |
| 4 Непосредственно после термообработки | 135,0 | 352 | 2 710 | 12 249 |
| 5 Через 1 сутки после термообработки | — | 15 424 | 21 [illegible] | 121 000 |
| 6 Через 22 суток после термообработки | — | 14 100 | [illegible] | 133 280 |

1) Specimen; 2) viscosity (in °VU) at; 3) before heat treatment; 4) immediately after heat treatment; 5) one day after heat treatment; 6) 22 days after heat treatment.

and is the greater the higher the treatment temperature. The viscosity of the mazout rose during subsequent storage and had been completely

restored after several days. In this case, distinctly expressed thixotropic properties appear in the paraffinic mazouts.

Knowledge of the viscosity-temperature properties of the mazouts and the effect of heat treatment on them enables us to apply technical skill to solution of problems related to the transfer, storage and preheating of mazouts under operational conditions.

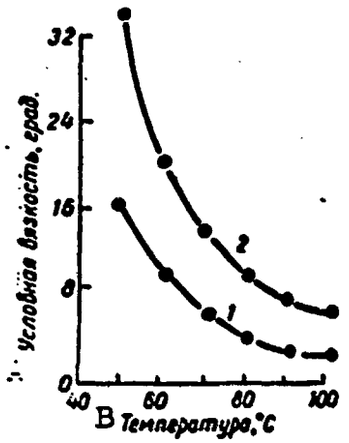


Fig. 174. Viscosity characteristic of watered fuel. 1) Dry boiler fuel; 2) boiler fuel with 15% water content. A) Conventional viscosity, degrees; B) temperature, °C.

Mazouts stored for the winter in railroad tank cars at oil dumps may assume the temperature of the outside air. Observations made by Ye.K. Smirnov [10] on the temperature drop in mazouts 40 and 80 in winter shipment in four-axle railroad tank cars that had been loaded at temperatures of +60 and +70° showed that after 110 hours en route, the temperature of both mazout grades was −10°, while after 230 hours it had become equal to the temperature of the outside air (−15°). At such low temperatures, the viscosities of mazouts reach rather high values (see Table 131) and drainage of the mazouts from the tanks can be effected only after preheating.

The heating temperatures recommended by G.M. Grigoryan [6] for mazouts to provide for drainage from railroad tank cars unfortunately do not take into account the influence of the heating temperature on the viscosity properties and pour points of the mazouts. To facilitate all subsequent operations performed in storage with the mazouts, it is necessary to heat them to 70-80°. At these temperatures, the influence of previous heat treatment is nullified and the viscosity-temperature properties of the mazouts are improved. In view of the fact that the

TABLE 133

Viscosities of Dry Watered Mazouts at Various Temperatures

| Мазуты 1 | 2 Содержание воды, % | 3 Вязкость (в °ВУ) при 75° | 50° | 30° | 20° |
|---|---|---|---|---|---|
| 4 Сернистый крекинг-мазут Ф-12, образец 1 . . | 6/в 9 | 4.35 | 12.1 | 46.4 | 147.2 |
| | 5 | 4.44 | 13.5 | — | 318 |
| 5 Сернистый крекинг-мазут Ф-12, образец 2. . . | 6/в | 3.98 | 11.2 | 53.0 | 161.4 |
| | 5 | 4.11 | 11.7 | — | 273.4 |
| 6 Сернистый крекинг-мазут 20 . . . . . | 6/в | 5.68 | 19.0 | 109.5 | 572 |
| | 5 | 6.14 | 24.0 | 115.5 | 691.4 |
| 7 Сернистый мазут прямой гонки 40 . . . . . | 6/в | 8.56 | 25.3 | 125.9 | 494 |
| | 5 | 9.64 | 32.4 | — | 594.7 |
| 8 Малосернистый мазут прямой гонки 40 . . . | 6/в | 5.91 | 23.6 | 136.4 | — |
| | 5 | 5.96 | 24.6 | 161.8 | — |

1) Mazout; 2) water content, %; 3) viscosity (in °VU) at; 4) F-12 sulfurous cracking mazout, specimen 1; 5) F-12 sulfurous cracking mazout, specimen 2; 6) sulfurous cracking mazout 20; 7) sulfurous straight-run mazout 40; 8) low-sulfur straight-run mazout 40; 9) dry-watered 5.

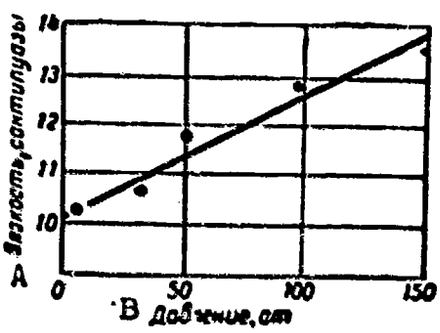


Fig. 175. Viscosity of cracking residue as a function of pressure. A) Viscosity, centipoises; B) pressure, atmospheres.

oil heaters used to preheat the mazout in draining it from the tank cars are not capable of delivering such high temperatures quickly, it is advisable to accomplish this preheating in a neutral tank.

The viscosities of mazouts vary as functions of their water content. Watering mazouts to 2-3% has virtually no influence on viscosity. Mazouts containing up to 5% of water show a viscosity increase particularly sharply at temperatures of 30° and below (Table 133). The viscosities of cracking mazouts increase to greater degrees on watering than do those of straight-run mazouts. The greater the water content in the mazouts, the more significant is the viscosity increase. Figure 174 presents viscosity-temperature curves for dry cracking mazouts and cracking mazouts containing up to 15% of water

[11]. In this case, the viscosity of the watered mazout had increased by a factor of approximately 6 even at 50°. As the temperature drops, the difference between the viscosities of dry and watered mazout becomes even more striking.

The viscosity of a petroleum product also depends on the pressure to which it is subject. Viscosity rises with increasing pressure. At very high pressures, the viscosity may increase quite significantly.

Z.I. Geller [12] studied the influence of pressure on the viscosity of cracking residues in the pressure range from 1 to 20 atmospheres at temperatures from 104 to 151° and in the pressure interval from 1 to 150 atmospheres at a temperature of 175° (Fig. 175).

The data obtained indicated that at pressures from 15-20 atmospheres, which are normally used in steam-boiler fireboxes for mechanical atomization of the fuel, the viscosities of cracking residues increase by 2.5-3.5% as compared with the viscosity at atmospheric pressure.

In analyzing the atomization process and in calculations for the design of heat-exchange apparatus, this viscosity increase may be omitted from consideration, since the absolute viscosity of mazout changes only insignificantly at high temperatures.

Surface Tension

Like viscosity, surface tension exerts considerable influence on atomization quality and the completeness of combustion of liquid boiler fuels. The surface tension is the force (ergs/cm$^2$ or dynes/cm) with which a liquid resists an increase in surface area. The higher the surface tension, the larger the size of the fuel droplet sprayed from the nozzle, the more difficult does it become to achieve fine atomization and good mixing of the fuel with air, and the poorer the combustion of the fuel. The incompleteness of combustion that is ob-

served results in smoking, formation of carbon black, and deposition of coke on the waterheating tubing of the boiler, so that the efficiency of the installation declines and fuel consumption increases.

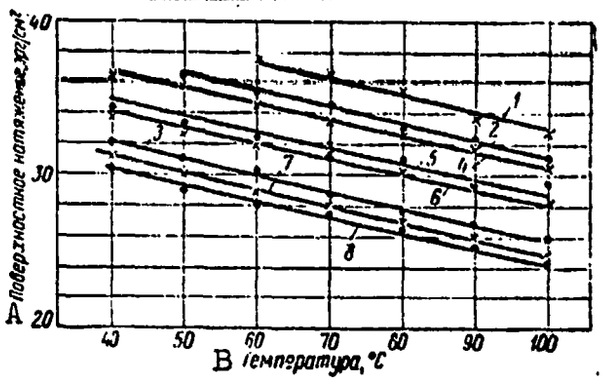


Fig. 176. Curves showing surface tension of mazouts as a function of temperature. 1) Sulfurous firebox (cracking) mazout, $VU_{50}$ = = 60; 2) same, $VU_{50}$ = 20; 3) same, $VU_{50}$ = 14.1; 4) sulfurous fleet (cracking) mazout, $VU_{50}$ = 12.0; 5) same, VU = 11.4; 6) straight-run sulfurous fleet mazout, $VU_{50}$ = = 4.38; 7) same, $VU_{50}$ = 4.48; 8) low-sulfur fleet mazout, $VU_{50}$ = 12. A) Surface tension, ergs/cm$^2$; B) temperature, °C.

Surface tension depends on a number of factors, most important among which are the temperature and nature of the liquid and of the phases in cont ct with it. For liquid boiler fuels, surface tension is a linear function that diminishes with increasing temperature. The surface tension of mazouts diminishes much more slowly with increasing temperature than does their viscosity for the same temperature increase. Normally, viscous mazouts possess higher surface tensions (Fig. 176) than low-viscosity mazouts. This difference is small and not as striking as might be expected on the basis of the mazout viscosities. Comparison of two mazout grades, a viscous grade with $VU_{50}$ = 20 and a

low-viscosity grade with $VU_{50}$ = 4.38, indicates that while the 50° viscosity of one mazout exceeds that of the other by a factor of 5, the surface-tension difference between these mazouts is no greater than 9%. According to Z.I. Geller [12], the surface tension of high-viscosity cracking residues diminishes by 4-4.5% as the temperature is raised from 90° to 120°, while their viscosities decline by a factor of 3-5. There is no single-valued relationship between viscosity and surface tension, and sometimes a lower-viscosity mazout has a higher surface tension than a mazout with higher viscosity. This indicates that the surface tension of boiler fuels also depends on their chemical composition, i.e., on the presence of polar compounds (oxygen, sulfur and nitrogen compounds).

Pour Point.

The pour point of liquid boiler fuels is usually taken as the basic parameter indicating the lowest temperature at which mobility of the fuel is ensured together with the possibility of draining and transferring it without previous warming.

The pour points of mazouts depend on the chemical nature of the raw material, the extent to which the light fractions have been extracted from the raw material, and the production method (straight distillation or cracking). The pour points of straight-run mazouts produced from paraffinic petroleums are usually much higher than those of mazouts produced from naphthenoaromatic petroleums. Increasing the "depth" to which the raw material is refined and the viscosities of the mazouts has the effect of raising their pour points.

It is necessary to note that the pour points of mazouts as determined by the standard method give only a relative conception of this characteristic of the fuel and may differ sharply from the actual pour point of the product under operational conditions. This is ac-

counted for by the fact that the pour points of mazouts depend to a considerable degree on heat-treatment conditions, i.e., on the heating temperature, the duration of heating, and cooling rate.

It has long been known that the pour point of a mazout depends on the extent of previous heating, although the laws involved in this phenomenon have not been exhaustively studied. Heat treatment has a sharp effect on the temperature at which the mazout loses mobility (solidifies).

Depending on the previous heating temperature of a mazout, it may lose mobility at both high and low temperatures, i.e., it may have both maximum and minimum pour points.

Maximum pour points may be reached in various grades of mazouts with prior heating temperatures from 30 to 70°, depending on chemical composition and production process. (Only the standard method of determining the pour points of mazouts provides for preliminary heating to 50°.)

Paraffinic mazouts are characterized by a maximum increase in pour point after heating to 60-70°. In cracking mazouts, it appears at lower treatment temperatures (20-30°).

Increasing the treatment temperature of paraffinic and cracking mazouts lowers the pour point. The minimum pour point can be produced by heating the mazouts to 80-100°.

Fleet mazouts, and particularly those produced from sulfur-bearing petroleums, are also liable to the influence of prior heat treatment. Low-sulfur mazouts have maximum pour points whose values are usually negative after heat treatment at 50-60°. Their minimum pour points occur after heating to 70-90°. Heat treatment has no influence on fleet mazouts with pour points of −28° and lower (defined in accordance with GOST). The straight-run sulfurous fleet mazout FS-5 usually

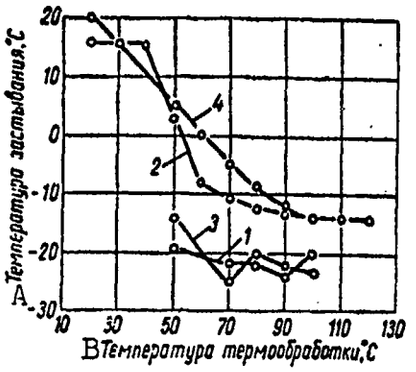


Fig. 177. Pour point of mazouts as a function of prior heating temperature. 1) Low-sulfur mazout, $VU_{50}$ = 12 (pour point −19°); 2) sulfurous cracking mazout, $VU_{50}$ = 12 (pour point +3°); 3) straight-run sulfurous mazout, $VU_{50}$ = 4.38 (pour point −14°); 4) sulfurous cracking mazout, $VU_{50}$ = = 12.8 (pour point +5°). A) Pour point, °C; B) heat-treatment temperature, °C.

has its maximum pour point after heating to 40-50°, and the corresponding figures for sulfurous cracking mazout are 20-30°. With rising heating temperature, the pour points of cracking mazouts drop off quite consistently and reach their minimal values after heating to 90-100° (Fig. 177). Raising the heating temperature of the mazouts further to 130-150° has no influence on pour point. The duration of heat treatment also has a noticeable influence on pour point.

As shown by the data listed in Table 134, increasing the preliminary heating time results for a number of mazouts in a sharp drop in pour point.

The above effects in which the pour points of mazouts depend on heat treatment are associated with the presence in the mazouts of solid hydrocarbons with various melting points and tarry [gummy] substances.

If the prior-heating temperature of mazouts has been lower than the melting point of the highest-melting paraffins, the crystals of these paraffins become crystallization centers during subsequent cooling and sharply accelerate the formation of structure, with solidification as a result.

When mazouts are heated to 90-100°, all solid paraffins are completely melted, and this inhibits subsequent structure formation; the pour point is found to be much lower. Increasing the heating time ensures more thorough melting of solid components.

TABLE 134

Influence of Duration of Heat Treatment at 70° on Pour Point

| 1 Мазуты | Температура застывания по ГОСТ, 2 °С | Температура застывания при 3 термообработке в течение | |
|---|---|---|---|
| | | 4 2 час. | 6 час. |
| 5 Сернистый крекинг-мазут 12 . . . | −6 | −14 | −20 |
| 6 То же . . . . . | −9 | −12 | −25 |
| » . . . . . | −5 | −9 | −23 |
| 7 Сернистый крекинг-мазут 20 . . . | +4 | −1 | −8 |
| 8 Малосернистый мазут 12 . . . . . | −18 | −20 | −26 |
| 6 То же . . . . . | −20 | −28 | −30 |
| » . . . . . | −19 | −22 | −26 |
| » . . . . . | −30 | −30 | −30 |

1) Mazout; 2) GOST pour point, °C; 3) pour point after heat treatment for; 4) hours; 5) sulfurous cracking mazout 12; 6) same; 7) sulfurous cracking mazout 20; 8) low-sulfur mazout 12.

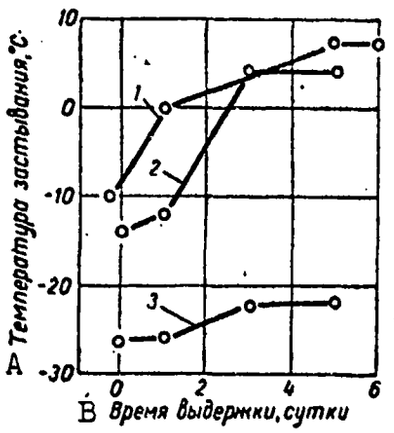


Fig. 178. Change in pour points of mazouts over time. 1) Sulfurous cracking mazout treated at 70° for 30 min; 2) same, for 2 hours; 3) low-sulfur F-12 mazout treated for 2 hours at 70°. A) Pour point, °C; B) holding time, days.

The processes described are complicated by adsorption of tarry asphaltic substances onto the paraffin; these inhibit the formation of large paraffin crystals.

Like its viscosity, the pour point of a mazout after heat treatment (70-100°) is not stable, and the mazout recovers its original pour point during subsequent storage.

Figure 178 shows how restoration of the pour points progresses during time for mazouts that have been subjected to heating to 70° and 100°. Full restoration takes place after 3-5 days. The rate of recovery depends on the proportions and interaction of solid paraffins and gummy substances, whose adsorption processes are quite diversified and depend in many respects on storage conditions and the rate of

cooling of the mazout after previous heating.

For a given pour point in a mazout, the cooling rate after heating is also of importance. The pour point is found to be much higher after rapid cooling than after slow cooling.

Problems of pour-point constancy in mazouts are of very great operational importance, since the pour point may be changed as a result of heating of the mazout for drainage or pump transfer. Consequently, pour-point data must be approached with caution, since the possibility of obtaining disagreeing values in determining the pour point for a given mazout specimen is not excluded, and this is an important concern for the supplier and user.

Despite all the above reservations, the pour point is an important technical constant of a boiler fuel for a given set of conditions. The method of heating the tanks and mazout pipelines, the method of shipping and draining the fuel, and other procedures are selected in accordance with pour point. It must be remembered, however, that the viscosity value at low temperature provides a much more complete characterization of the fuel's behavior than does the pour point.

The pour points of fuels must be determined after dehydration, since the presence of water – particularly in the case of low-viscosity mazouts – affects the correctness of the determination. This will be seen from the following figures.

| | | | | | |
|---|---|---|---|---|---|
| 1 Содержание воды в мазутах, % . . . . . | 0 | 0,5 | 1 | 2 | 5 |
| 2 Температура застывания, °С . . . . . | −5 | −4 | 0 | +2 | +2 |

1) Water content in mazouts, %; 2) pour point, °C.

Flash Point

Flash point is an index for liquid boiler fuels that enables us to draw inferences as to the fire hazard. This index acquires par-

ticular importance for fuels used in marine installations, where they are stored in proximity to crew's quarters and the boiler installations. Consequently, the flash point is determined in a sealed instrument for fleet mazouts, which are basically intended for marine installations, and is set at 80° for FS-5 and 90° for F-12 and F-20.

The flash point obtained from closed-instrument determinations is usually 30-40° lower than that obtained in an open instrument, since in the former case combustible vapors accumulate in the crucible.

Cracking mazouts, and low-viscosity cracking mazouts in particular, are frequently characterized by lower flash points (closed-crucible determination) because of their content of volatile composition products, which disperse in an open instrument before there is enough of them accumulated for ignition, so that the difference in the determinations may be as high as 70°.

In shipping and storage, the flash points of cracking mazouts normally rise considerably.

For the firebox mazouts used in stationary boiler installations, flash points up to 140° are tolerated, depending on the fuel grade, and are determined in the open instrument.

It has been established by N.I. Chernozhukov and A.M. Guttsayt that the flash points of mazouts are usually somewhat lower under conditions of tank storage than those determined by the standard method and depend on the tank capacity and the extent to which it is filled. For this reason, it is recommended that the mazouts be heated to 10-20° below the flash point when they are warmed up in open (unpressurized) tanks. In closed spaces that are under pressure (oil preheaters, coils, tubing), a mazout may be heated up above the flash point.

The mazout must first be dehydrated for a flash-point determination, since even a minor quantity of water present in the fuel de-

presses the actual flash-point value noticeably; with large water contents, the entire mass of mazout is ejected.

Tarry Substances

The tarry substances present in boiler fuels are quite detrimental to their properties and complicate the conditions of operation with them. The presence of tarry substances in mazouts is associated with a loss in their stability, disturbance of the combustion process, and the formation of water-and-mazout emulsions. Unfortunately, the content of tarry substances in boiler fuels is to this day regulated only for fleet mazouts and is determined by the asphalt tars. However, the asphalt tars are a poor characteristic for the actual tar content in the fuels and do not indicate the type of tarry substances present. This last piece of information is particularly necessary, since the tars, asphaltenes and carbenes present in the mazouts with carboids (Table 135) influence their properties in different ways. With knowledge of the "itemized" content of tarry substances, we may evaluate the behavior of mazouts under operational conditions in advance.

It is convenient to use the cokability index of mazouts to obtain some preliminary evaluation of boiler fuels as regards the reliability with which the firing process can be conducted, as well as the stability of the fuels in storage. This quantity characterizes the total content of tarry substances to a much greater degree than do the asphalt tars. The cokability may also be used for tentative judgments as to the fuel's content of asphaltenes, which have the most severely detrimental influence on the properties of the fuels: the greater the asphaltene content, the higher the cokability. Cracking mazouts are distinguished from straight-run mazouts by having higher asphaltene contents, as well as higher contents of carbenes and carboids. The content may run as high as 14-15% in heavy, high-viscosity

cracking mazouts.

TABLE 135

Content of Tarry Substances in Mazouts

| 1 Мазуты | 2 Смолы, % | 3 Асфальтены, % | 4 Карбены и карбоиды % | 5 Акцизные смолы, % | 6 Коксуемость, % |
|---|---|---|---|---|---|
| 7 Крекинг-мазут 12 (сернистый) | 10,59 | 4,30 | 0,19 | 40 | 10,22 |
| 8 Крекинг-мазут 40 . . . . . | 8,12 | 6,64 | 1,32 | 72 | 15,20 |
| 9 Сернистый мазут прямой гонки ФС-5 . . . . . | 13,60 | 0,94 | 0,03 | 28 | 7,97 |
| 10 Малосернистый мазут прямой гонки Ф-12 . . . . . | 14,03 | 0,11 | 0,03 | 28 | 5,79 |
| 11 Крекинг-остаток (мазут 200) [12] . . . . . | 16,60 | 14,5 | 1,19 | — | 17,60 |

1) Mazout; 2) tars, %; 3) asphaltenes, %, 4) carbenes and carboids, %; 5) asphalt tars, %; 6) cokability, %; 7) cracking mazout 12 (sulfurous); 8) cracking mazout 40; 9) sulfurous straight-run FS-5 mazout; 10) low-sulfur straight-run F-12 mazout; 11) cracking residue (mazout 200) [12].

Fuels with high tarry-substance contents are usually unstable and incompatible. During storage and on heating, an unstable fuel may also form and precipitate tarry deposits, which may contain mechanical impurities and water, entrained oil and solid paraffins.

The instability of boiler fuels is accounted for by a number of causes: the presence of asphaltenes in the fuel in a colloidal dispersed state from which they may coagulate; by the formation of large tarry particles as a result of chemical changes (oxidation and polymerization) of the tars and asphaltenes during storage and heating, which promotes formation of the precipitate; by the discrepancy between the densities of the fuel and the tarry substances (asphaltenes 1.07-1.10, carboids 1.27-1.30), particularly on heating, when the viscosity of the fuel drops simultaneously, thus accelerating the settling of solid particles.

Furthermore, solid carbon-bearing particles (carbenes and carboids) which settle rapidly into the precipitate, act simultaneously

as centers for coagulation of the asphaltenes and accelerate their precipitation.

During storage of boiler fuels and the periodic warming to which they are subjected, tarry deposits settle out rapidly. According to M.F. Nagiyev [12], 23.6% of the carbenes and carboids precipitate in 5 hours at a temperature of 120°, and as much as 97% in 22 hours at 250°.

When mazout 100 is stored for 90 hours with periodic warming in the 80-85° range, the quantity of solid impurities near the bottom and on the heating coils is doubled [14].

Deposits may also settle out of boiler fuels on dilution of heavy fuels with light fuels, or on addition of heavy fuels with higher tarry-substance contents to a light fuel. In this case, we speak of incompatibility of the fuels [15, 16].

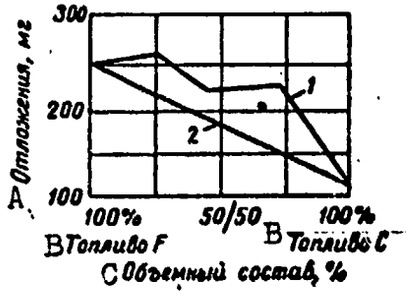


Fig. 179. Incompatibility of residual boiler fuels on mixing. 1) Actual data; 2) calculated data. A) Deposits, mg; B) fuel; C) composition by volume, %.

Practical experience with boiler fuels has shown that stable boiler fuels are usually compatible. However, more precipitate frequently forms in mixtures of high-viscosity fuels during storage than would be expected on the basis of the stabilities of the individual fuels. Figure 179 shows the stability of a mixture of two boiler fuels (F and C) [16]. One of the fuels used in the mixture gives 250 mg of deposit, while the other produces little more than 100 mg. When they are mixed in various proportions, the amount of sediment formed is larger than would be expected.

Fuel incompatibility is of particular importance for seagoing vessels because of the possibility that they may be fueled with dif-

ferent fuels at their numerous ports of call. These fuels may differ from one another over a very wide range of chemical composition, so that cases in which significant quantities of sediment are formed on mixing become possible.

Sediments that have formed reduce the useful space inside tanks and bunkers, reduce the efficiency of heat transfer across the heating surfaces of steam preheaters, and clog fuel filters, mazout lines, and oil preheaters. All this affects normal operation with them.

Secondary natural dispersion of sediments that have formed from boiler fuels does not take place, and this process can hardly even be conducted artificially.

Propeller-type agitators are installed abroad at tank bottoms to prevent sedimentation; during operation, these hold the asphaltene-carboid admixtures present in the fuel in a suspended state. The proposed circulation-heating method for fuels used on seagoing vessels also has the same objective in view [14].

The most expedient method, and the one most worthy of its name, is that of raising the stability and compatibility of fuels by introduction of additives. The polymer dispersing additives used for this purpose not only inhibit the growth of tar particles and prevent their sedimentation, but also disperse and eliminate sediment that has already formed.

The additives also improve the firing process. The presence of tarry substances in the mazout and formation of sediment result in their accumulation in the form of a solid scale at the injector nozzle, and the channels in the core may become clogged so that the feed of mazout is completely cut off. Intensified sparking is also noted simultaneously with combustion of fuels having high tar contents.

The detergent additive introduced into the fuel prevents fouling of the nozzles, reduces sparking and allows the fuel to burn more completely. In the Soviet Union, tests of the vnii np-102 additive, which is of this type, have given positive results.

Water in Fuel

Water present in a boiler fuel lowers its heat of combustion, increases the consumption of fuel and reduces the efficiency of the boiler installation. In addition, this water activates the accumulation of sediment on the bottoms of fuel tanks and upsets the combustion regime of the fuel. Nonuniform distribution of water in the mass of the fuel (in layers or in isolated pockets) may extinguish nozzles and even result in explosions in the firebox, thus putting the boiler out of operation.

Moisture in mazouts – and sulfurous mazouts in particular – contributes to accelerated corrosion of tanks, pipelines, pumps and the like and intensifies corrosion of the boiler's heating surface by the smoke gases due to the increase in their moisture content.

In naval vessels, watering of the mazouts also results in a drop in the cargo-carrying capacity and range of the vessels. Cases of rupture of double-bottom tanks when watered mazouts are heated are possible as a result of their violent bumping.

In the metallurgical industry, a water content in the mazouts reduces the skimming of steel and prolongs the smelting cycle. For this reason, the technical specifications limit the admissible water content in fleet mazouts to 1%, and that in firebox mazouts to 5%. The petroleum refineries produce mazouts that satisfy these specifications and contain no more than 1-2% of water. In practice, however, the mazouts are frequently delivered to the nozzles of boiler installations with higher water contents. The basic cause of mazout watering

is the live-steam procedure used in preheating them to make possible and then accelerate drainage of the mazouts from railroad tank cars and petroleum barges, especially during the winter.

The widespread use of live steam to preheat mazouts is accounted for by the simplicity of the method and its high effectiveness. The steam is fed through perforated pipes or nozzles directly into the mazout, where, condensing, it gives up all of its heat. As a result of live-steam heating, low-viscosity mazouts are watered to 4-12% [9, 17], and high-viscosity firebox mazouts to 20-30% [14, 18], depending on the temperatures of the mazout and the air, the viscosity of the mazout, and the temperature and pressure of the steam.

Mazouts may also be watered during water transport as a result of leaks in oil barges and seagoing vessels, during storage in underground tanks, during surface heating, when steam gets into the mazouts through defective heating coils, and as a result of other causes.

The most severe watering of mazouts takes place when railroad tank cars, petroleum barges and tanks are thoroughly cleaned of residues with the use of live steam. In this case, the watering of the so-called mazout washings may rise as high as 50-75% [18] and higher.

Hydrophobic emulsions of the "water in oil" type form as a result of mixing of water with mazout. The dispersion medium is the mazout, in which the water is distributed in the form of extremely fine droplets. The higher the dispersion of the emulsion, the more stable it becomes. In turn, the dispersion of the emulsion depends on the viscosity and density of the mazout, the degree to which water is mixed with the mazout, and the quantity and nature of the emulsion stabilizers (emulsifiers).

When water contaminates mazout during transportation or storage, water-mazout emulsions are formed only when the water and mazout are

vigorously agitated (in storage reservoirs, during transfers, and in ship tanks during heavy seas). On mixing with water, low-viscosity mazouts form water-mazout emulsions much more rapidly than high-viscosity mazouts, although the emulsions formed in either case are usually easily broken up by heating and allowing to settle.

The emulsions obtained when mazouts are heated with live steam are distinguished by higher stability than the emulsions formed by mixing water and mazout. This is accounted for by the higher degree of dispersion due to the excellent contact between the water and mazout. In this case, the stability of the emulsions depends on the quantity and effectiveness of the emulsion stabilizers present in the mazouts. It was established by B.V. Losikov and the author [9] that the stabilizers of water-mazout emulsions are usually asphaltenes and, sometimes, gums. The influence of asphaltenes on the stability of water-mazout emulsions may be seen from Table 136. A cracking mazout containing 4.3% of asphaltenes and watered to 15% by live steam forms a stable emulsion that does not separate on prolonged standing and heating to 70°.

After removal of the asphaltenes, the mazout no longer forms a stable emulsion and separates completely from the water. On introduction of asphaltenes extracted from cracking mazout into a low-sulfur mazout, the latter forms an emulsion that yields nothing to the emulsion of sulfurous cracking mazout as regards stability. The stabilizing action of asphaltenes on water-mazout emulsions is accounted for by the fact that the asphaltenes, which are present in a colloidally dissolved state in mazouts and possess differing wettabilities by water and hydrocarbons, are readily adsorbed on the water-mazout interface and form dense armoring films that prevent individual drops of water from fusing into larger drops; as a result, settling

the water from the mazout emulsion is inhibited and the stability of the emulsion is raised.

TABLE 136

Influence of Asphaltenes on the Stability of Water-Mazout Emulsions

| 1 Мазуты | 2 Выделялось воды после 24 час. отстоя при 70°, % |
|---|---|
| 3 Сернистый, крекинга, $ВУ_{50}=12$ . . | 4 Эмульсия не расслаивается |
| 5 Малосернистый, прямой перегонки, $ВУ_{50}=12$ . . . . . | 60 |
| 6 Сернистый, крекинга, без асфальтенов . . . . . | 100 |
| 7 Малосернистый, без асфальтенов . | 100 |
| 8 Малосернистый + асфальтены сернистого . . . . . | 4 Эмульсия не расслаивается |

1) Mazout; 2) water separated after 24 hours of standing at 70°, %; 3) sulfurous, cracking, $VU_{50} = 12$; 4) emulsion does not separate; 5) low-sulfur, straight-run, $VU_{50} = 12$; 6) sulfurous, cracking, without asphaltenes; 7) low-sulfur, without asphaltenes; 8) low-sulfur plus sulfurous asphaltenes.

Despite the fact that the sizes of the water globules in emulsions usually vary over a wide range – from those that are barely discernible under the microscope to large inclusions, the dispersion of the water drops is considerably greater in the emulsions of sulfurous mazouts, and the cracking mazouts in particular, than in low-sulfur mazouts (Fig. 180), and, consequently, the stability of the emulsions will also be considerably higher.

Together with the asphaltenes, the tars also function as stabilizers of water-mazout emulsions, but to a considerably lesser degree. The above is not contradicted by the data of B.P. Tonkoshkurov et al. [20], according to whom the formation of emulsions in petroleums is associated with the stabilizing action of asphaltenes and tars.

Consequently, as a result of their elevated asphaltene contents, sulfurous mazouts (see Table 135) form the most stable emulsions,

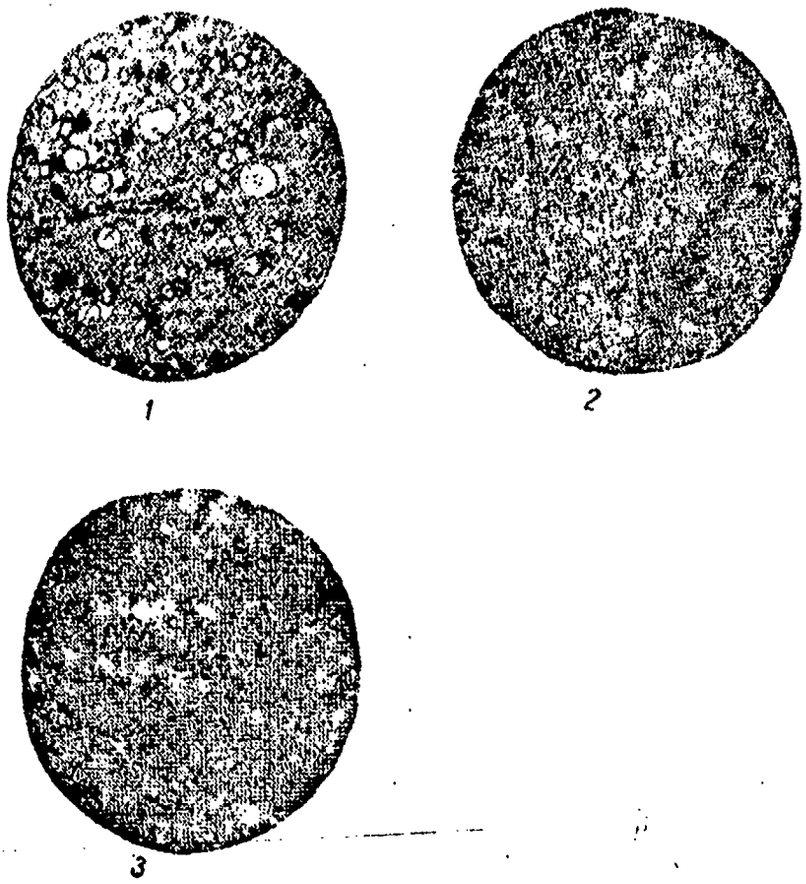


Fig. 180. Water-mazout emulsions formed during heating of mazout by live steam. 1) Low-sulfur mazout, straight run, $VU_{50}$ = 12; 2) straight-run sulfurous mazout, $VU_{50}$ = 4.38; 3) sulfurous cracking mazout, $VU_{50}$ = 12.

which are difficult to separate by the usual standing-and-heating procedure. The rate of separation of water is considerably lower in a sulfurous straight-run mazout than in a low-sulfur product; here, the water is separated in small quantities from the water-mazout emulsions and the water that has not separated descends from the top of the mazout to become distributed in layers, with the maximum content in the lower layer (up to 70%) [9].

In sulfurous cracking mazouts, the emulsion remains virtually undisturbed and the water does not settle out. High-viscosity firebox mazouts stand free of water particularly poorly. The factors that complicate dewatering of the mazout in this case are the high viscos-

ities of the mazouts and the minor difference between the densities of the mazout and water.

At high temperatures (110-160°), when high-viscosity mazouts show minimal and practically constant viscosity, settling of the water is prevented by the very small difference between the specific gravities of the water and the mazout, and at temperatures below 100° the water does not separate due to the high viscosity of the mazouts (Fig. 181). As a result, the settling rate of water droplets from firebox-mazout emulsions is not the same for different grades, and at a given temperature the settling rate of water droplets in low-viscosity mazouts is considerably higher than in high-viscosity products. The settling rate of the water changes with changing temperature. A diagram showing the settling rate of water droplets with d = 0.09 mm as a function of density and temperature for mazouts of various grades is given in Fig. 182.

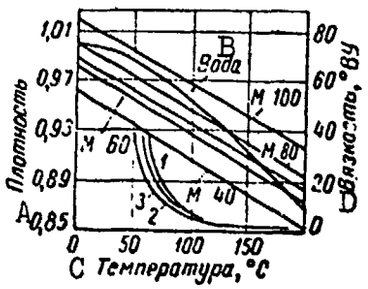


Fig. 181. Density as a function of temperature for water and mazouts of various grades [26]. 1, 2, 3) Viscosity curves of grade 80, 60 and 40 mazouts. A) Density; B) water; C) temperature, °C; D) viscosity, °VU.

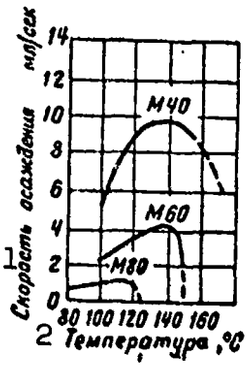


Fig. 182. Rate of settling of water droplets with d = = 0.09 mm as a function of temperature [26]. The figures on the curves denote the grades of mazout. 1) Settling rate, ml/sec; 2) temperature, °C.

It has been established that the most effective dewatering of grades 40 and 60 firebox mazouts is achieved at temperatures of 110-

140°, and for grades 80 and 100 at 210°. Here, the water must be separated at high pressures (up to 25 atmospheres for grade 100 mazout) [19].

Special and expensive equipment that is not at the disposal of many storage facilities and oil dumps is required to observe this condition. Consequently, it is necessary to take all measures in shipping, draining and using mazouts to hold watering to the lowest possible minimum.

Many methods and techniques have been suggested to prevent watering of mazouts when they are drained from railroad tank cars during the winter. The most frequently encountered practical approach is preheating of the mazouts by portable coil heaters. However, the cumbersomeness and great weight of the latter make it difficult to use them, since insertion of the coils in the railway tank cars requires special gantries and hoist mechanisms. The basic shortcoming of the portable coil elements, however, is the inadequate heating efficiency, which results from the low heat-transfer coefficient (40-50 kcal/$m^2$·hour·°C for high-viscosity petroleum products and 100-120 kcal/$m^2$·hour·°C for low-viscosity products) [22]. Increasing the heat-dissipating surface simply increases the size and weight of the preheater. For example, the N548-51 heater has a total heating surface of 23.2 $m^2$ and weighs 228 kg [23].

Proposals to raise the heat-transfer coefficient by replacing series coils by coils having turns operating in parallel, which would accelerate drainage by a factor of 4 [21], and by the use of vibrating or, more precisely, swinging preheater elements, which would raise the heat-transfer coefficient by a factor of 20 (900 kcal/$m^2$·hour·°C) have not come into practical use as yet.

Tank cars are equipped with steam jackets for most efficient

drainage of mazout (without watering and without layovers for the tank cars). However, the number of specially equipped tank cars is thus far quite small. With this unloading method, the mazout itself is not actually preheated; only a surface layer of it is liquefied. Consequently, drainage of a viscous mazout into a storage tank requires steam jacketing of the drainage troughs and gutters and headers; it is also necessary to have the headers inclined slightly toward the receiving reservoir. The presence of a receiver with this drainage method is absolutely necessary, since the mazout is warmed in it for subsequent pump transfer into the actual storage tank. Installation of the auxiliary equipment is impeding and delaying the introduction of this drainage method.

One of the most effective countermeasures against water-mazout emulsions is the use of deemulsifiers. The deemulsifiers Typol, Calsoline and others are used abroad to break up water-mazout emulsions [24].

This method is well known and used to dewater and degum sulfurous petroleums [25, 26].

It was noted earlier that mazouts form hydrophobic emulsions with water. Emulsions of this type can be broken up with substances that possess distinct hydrophilic properties. Reaching the water-mazout interface, these substances are capable of lowering surface tension and weakening and breaking up films and envelopes. The principle on which they work in breaking up emulsions is based on phase inversion.

With the objective of finding deemulsifiers for breaking up water emulsions of sulfurous mazouts, the author and I.V. Golovistikov investigated a number of products possessing hydrophilic properties. It was established that the most active deemulsifiers were the substances given the names OP-7 and OP-10 (TU 3554-53) and sodium salts of sulfoxy

acids (alkaline wastes formed in acid-alkali purification of oily petroleum distillates (TU 330-48).

Table 137 lists laboratory data on the destruction of a stable sulfurous cracking-mazout emulsion by deemulsifiers. As will be seen from the table, the introduction of 0.25% of the OP-7 deemulsifier into the emulsion makes it possible to eliminate water to the required GOST standards by settling and heating to 70°.

Tests of the OP-7 deemulsifier under industrial conditions (OP-7 concentration 0.25%, standing at 50°) confirmed its high quality.

It is advisable to introduce deemulsifiers into mazouts prior to watering and formation of emulsions, i.e., at the points of production, since in this case their effectiveness is higher than when they are added to a water-mazout emulsion.

TABLE 137

Effectiveness of Deemulsifiers (settling at 70°)

| 1 Деэмульгаторы | 2 Содержание деэмульгатора, % | 3 Время отстоя, часы | 4 Количество воды | | | 8 Содержание воды в мазуте после отстоя, % | |
|---|---|---|---|---|---|---|---|
| | | | 5 введено в мазут, см³ | 6 выделилось | | | |
| | | | | 7 см³ | % | 9 верх | 10 низ |
| 11 Без деэмульгатора . . . . | 0 | 48 | 15 | — | — | 12 Отсутствуют | 16,0 |
| 14 С деэмульгатором ОП-7 . . | 0,1 | 34 | 18 | 11 | 61 | — | 1,8 |
| | 0,25 | 16 | 12 | 10 | 85 | 13 Следы | 0,73 |
| | 0,5 | 4 | 12 | 10 | 85 | 12 Отсутствует | 0,7 |
| 15 Щелочные отходы . . . . | 0,25 | 36 | 16 | 11 | 44 | 2,6 | 2,6 |
| | 0,5 | 36 | 19 | 17 | 89 | 0,8 | 0,6 |

1) De-emulsifier; 2) de-emulsifier content, %; 3) settling time, hours; 4) quantity of water; 5) introduced into mazout, $cm^3$; 6) separated; 7) $cm^3$; 8) water content in mazout after settling, %; 9) top; 10) bottom; 11) without de-emulsifier; 12) none; 13) traces; 14) with OP-7 de-emulsifier; 15) alkaline wastes.

Recently, a technique in which heavily watered high-viscosity mazouts and mazout washings are used without preliminary dehydration

as firebox fuels for stationary boilers has acquired importance.

Stable combustion of watered high-viscosity mazouts is achieved by creating a water-mazout emulsion with uniform distribution of the water through the entire volume of fuel. The "water-oil" type of emulsion is created by the use of a high-speed mechanical disperser [11] or by blasting live steam (compressed air) through the mazout [18].

B.V. Kantorovich et al. [11] account for the possibility of burning heavily watered mazouts (to 30%) by the specific nature of combustion of the water-fuel emulsion. Due to the differing boiling points of the water and the mazout, emulsion droplets undergo so-called "microexplosions" at high temperature in the combustion zone, with the result that extremely fine secondary shattering of the fuel takes place, improving mixing with air. This reduces the loss of heat with the flue gases and partially offsets the expenditure of heat on vaporizing the water present in the fuel.

With water contents above 30% in the emulsion, combustion deteriorates noticeably, the boiler's efficiency drops off, and its steam output is lowered as a result of the smaller quantity of mazout entering the firebox.

The proposed method of burning watered mazouts is not expedient for marine boiler installations, since it reduces sailing range considerably. Furthermore, due to the increased content of water in the fuel, corrosion of the heating surfaces would apparently be greatly intensified, particularly when high-sulfur fuels are burned.

Ash in Fuel

There is usually little ash present in liquid boiler fuels - from 0.01 to 0.5%. According to GOST requirements, the ash content in fleet mazouts may not exceed 0.15%, and that in firebox mazouts may not be higher than 0.3%.

Mazout ash consists primarily of salts transferred into the

mazouts during refining of the petroleum. Salts can be either partially dissolved in petroleum or be present there in a colloidal state (complex compounds of metals), or they may get into it together with the drilling muds. The composition and quantity of salts in mazouts vary depending on the salt content of the petroleums and the extent to which the salts were eliminated. Apart from salts originating from the petroleum, mazouts may also contain corrosion products of the refinery apparatus, this corrosion taking place particularly vigorously when sulfurous petroleums are processed.

The basic components in mazout ash are vanadium, sodium, calcium, aluminum, iron and nickel. Table 138 presents data obtained by the author on the ash composition of sulfurous and low-sulfur mazouts.

The tabulated data, which characterize the ash composition of the mazout specimens tested, provide a general idea of the composition of mazout ash. However, numerous detailed analyses of the ash component of various mazout grades have shown that the ash of sulfurous mazout and the ash of low-sulfur mazouts have nearly the same composition, and that the absolute ash contents are practically identical in either case. The basic difference in the sulfurous-mazout ash consists in the presence of vanadium, which is absent from low-sulfur mazouts or present in negligibly small quantities, and in an elevated sodium content. Straight-run fleet mazout contains up to 0.003-0.004% of vanadium. According to A.V. Kozhevnikov [28], sulfurous cracking mazouts contain up to 0.01% of vanadium; there is considerably more vanadium in firebox mazouts than in fleet mazouts. According to V.G. Nikolayeva et al. [30], mazout 20 has up to 0.007% of vanadium, mazouts of grades 40, 60 and 80 up to 0.012%, and cracking residues up to 0.020%.

Despite the low ash content in the liquid fuel, its combustion

on the outer heating surfaces of boiler installations results in formation of ash deposits that lower the reliability and economy indices of the installation's performance. In combustion of mazouts, the ash is deposited in the form of dense tough scales on the working surfaces of the boilers, the water-heating tubes, the steam superheaters, the economizers and the lining of the fireboxes and clogs the flues.

A special property of these deposits is their tendency to build up continuously on convective heating surfaces; this limits the service life of the boiler unit.

TABLE 138

Ash Composition of Sulfurous and Low-Sulfur Mazouts

| Показатели 1 | 2 Сернистый крекинг-мазут из смеси ставропольской, саратовской и бавлинской нефтей | 3 Сернистый прямогонный мазут из туймазинской нефти | 4 Мазут флотский из ильской нефти |
|---|---|---|---|
| 5 Сера, % | 2,2 | 1,8 | 0,6 |
| 6 Зола, % | 0,183 | 0,076 | 0,106 |
| 7 Анионы и катионы в минеральной части мазутов, %: | | | |
| Cl | 2,19 | 8,17 | 6,32 |
| $SO_4$ | 29,59 | 28,33 | 28,15 |
| Na | 1,91 | 3,05 | 8 Отсутствует |
| Ca | 16,11 | 27,93 | 27,62 |
| Mg | 2,50 | 6,73 | 5,55 |
| Ni | 0,74 | 1,05 | 4,28 |
| Mn | 9 Следы | 9 Следы | 0,06 |
| Fe | 1,04 | 8,71 | 14,44 |
| Al | 8,68 | 9,62 | 6,64 |
| V | 0,61 | 1,92 | 9 Следы |
| 10 Окислы в золе мазута, %: | | | |
| $Na_2O$ | 3,09 | 5,66 | 8 Отсутствует |
| CaO | 9,31 | 20,51 | 20,43 |
| MgO | 5,20 | 16,25 | 12,02 |
| $Fe_2O_3$ | 1,87 | 18,05 | 20,01 |
| $Al_2O_3$ | 20,42 | 26,27 | 17,00 |
| NiO | 1,18 | 1,03 | 7,65 |
| MnO | 9 Следы | 9 Следы | 0,12 |
| $V_2O_5$ | 1,38 | 4,03 | 9 Следы |
| $SiO_2$ | 57,35 | 6,45 | 12,77 |

1) Index; 2) sulfurous cracking mazout from mixture of Stavropol', Saratov and Bavlinskiy petroleums; 3) sulfurous straight-run mazout from Tuymazy petroleum; 4) fleet mazout from Il'skiy petroleum; 5) sulfur, %; 6) ash, %; 7) anions and cations in mineral part of mazouts, %; 8) none; 9) traces; 10) oxides in mazout ash, %.

The presence of large amounts of deposits on boiler heating surfaces gives rise to a number of complications in operation: heat-transfer conditions deteriorate, the flue-gas temperature rises, the temperature of the superheated steam and the steam output decline, the gas resistance is increased and, as a result, the efficiency of the boiler diminishes. Apart from the deteriorating heat exchange, ash deposits intensify corrosion of the metallic surfaces and break down the firebox lining [5, 27].

The basic sources of ash-deposit formation on the boiler heating surfaces are sodium and vanadium [5, 28, 32, 35]. In a study of the influence of individual residual-fuel components on refractory materials, Gones and Hardy [31] showed that salts of alkali and alkaline-earth metals lower the melting point of firebrick and form on its surface hard vitreous films that sometimes results in chipping of the firebrick.

In connection with the use of mazouts for gas turbines (operating temperatures at heating surfaces 700-800°), the authors of many papers [30-35] regard vanadium compounds as a particularly dangerous ash component – an agent that causes corrosion of metallic surfaces and contributes to the formation of deposits on heating surfaces. Vanadium compounds are not only corrosively aggressive but also bonding agents, since vanadium pentoxide, which forms on combustion of the mazout, sinters and melts at temperatures of 650-700°. Alkali-metal compounds in the form of sulfates also produce large amounts of deposits, but corrode noticeably only in the presence of $V_2O_5$. Vanadium-containing petroleum ash also attacks refractory materials vigorously [31], particularly in combination with sodium.

It has been established by research studies [34, 36] that the deposit formation and corrosion that appear at temperatures above 6[illegible].

are associated with the presence of vanadium. At lower temperatures, the chief cause of the deposits are sulfates (basically, sodium sulfate).

Analysis of deposits taken from various heating surfaces in boiler installations after operation of sulfurous and low-sulfur mazouts (Table 139) has shown that the basic components of the deposits are identical to the components of mazout ash. A characteristic property of all deposits is the absence of chlorides, despite the fact that the mineral impurities present in the mazouts contained large quantities of chlorides. The deposits consist predominantly of sulfates. It appears that in combustion of mazout, the ash chlorides decompose and the chlorine is replaced by sulfur from the fuel. The basic difference between the compositions of sulfurous and nonsulfurous mazouts consists in the vanadium content of the former, together with the elevated content of insoluble oxides, which interfere with cleaning of the tubes. It was indicated earlier that molten vanadium pentoxide is an active corrosive agent, although the danger of vanadium corrosion is not too great in boiler installations having the prevailing parameters, since the corrosive aggressiveness of vanadium comes into evidence basically at temperatures of 650° and upward.

In the use of boilers with high steam temperatures, vanadium corrosion will be just as severe as in the case of gas-turbine installations.

It is necessary to note that deposit analyses testify to the effect that corrosion processes take place under the deposit layer irrespective of the grade of mazout burned. Here, the corrosion process is apparently the result not so much of the action of sulfur or vanadium oxides as of moisture-condensation phenomena, which take place more actively on surfaces covered with deposits than on clean

Composition of Deposits Formed on Combustion of Sulfurous and Low-Sulfur Mazouts (in %)

| 1 Мазуты, сжигаемые в топке | 2 Место отбора проб | 3 Состав компонентов в отложениях | | | | | | | | | | | | | | | 6 | 7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 4 влага | 5 зола | $SO_3$ | Cl | K | Na | Ca | Mg | Fe | Ni | Cr | Mn | V | $SiO_2$ | Нерастворимые окислы | Органическая часть |
| 8 Сернистый крекинг-мазут (S = 1,9÷2,5%) | 9 Экранные* трубы | 1,5—5,6 | 8,0—27,3 | 6,4—41,9 | 12 Отсутствует | 0—0,8 | 1,3—17,2 | 1,9—10,2 | 12 Отсутствует | 1,0—19,6 | 0—2,0 | 12 Отсутствует | 14 Следы | 0,1—1,3 | 0,1—2,3 | 0,1—0,7 | 14,3—86,0 |
| | 10 Конвективные трубы | 0,8—4,5 | 68,4—96,8 | 23,5—60,6 | То же | 0—0,42 | 10,4—24,9 | 2,1—7,2 | То же | 1,2—3,6 | 1,4—4,5 | То же | » | 0,6—1,0 | 0,2—3,0 | 0,01—16,2 | 2,1—76,5 |
| | 11 Пароперегреватель | 2,9 | 84,2 | 57,4 | 13 » | Отсутствует 12 | 21,1 | 2,9 | » | 6,7 | 0,8 | 13 » | » | 1,25 | 5,5 | — | 6,5 |
| 15 Сернистый мазут прямой гонки (S=1,6÷1,84%) | 9 Экранные трубы | 4,5 | 13,1 | 6,6 | 14 Следы | 12 Отсутствует | 2,4 | 0,9 | 12 Отсутствует | 0,9 | 0,6 | 12 Отсутствует | 12 Отсутствует | 0,1—0,5 | 4,6 | 2,7 | 80,5 |
| | 10 Конвективные трубы | 1,7—3,6 | 59,1—86,5 | 42,0—48,5 | 0—0,14 | 0—0,9 | 12,1—19,2 | 0—1,9 | 0—0,4 | 0,4—10,9 | 0—0,8 | То же | 0—0,7 | 0,1—0,4 | 6,6—14,9 | 5,2—10,8 | 6,7—94,5 |
| | 11 Пароперегреватель | 4,2 | 66,9 | 21,7 | Следы 14 | Отсутствует 12 | 3,7 | 0,8 | Отсутствует 12 | 12,3 | 3,5 | 13 » | Следы 14 | 0,1—0,4 | — | 10,7 | 20,7 |
| 16 Малосернистый мазут (S=0,3÷0,66%) | 9 Экранные трубы | 0,7—4,5 | 17,3—31,0 | 8,2—36,0 | 12 Отсутствует | 0—1,0 | 0,1—12,4 | 0,7—4,6 | 0—0,7 | 1,0—4,1 | 0,04—0,4 | 12 Отсутствует | 14 Следы | 12 Отсутствует | 1,7—3,6 | 0,8—1,7 | 43,0—81,6 |
| | 10 Конвективные трубы | 0,3—11,6 | 40,1—93,3 | 27,9—61,8 | То же | 0—1,6 | 6,9—25,8 | 1,4—5,8 | 0,4—1,4 | 1,0—11,3 | 0,3—3,9 | То же | » | То же | 2,8—4,5 | 0,4—4,8 | 5,8—49,1 |
| | 11 Пароперегреватель | 11,7 | 78,0 | 35,9 | 13 » | Отсутствует 12 | 1,8 | 3,8 | Отсутствует 12 | 38,1 | 0,8 | 13 » | » | 13 » | 1,7 | 1,3 | 13,7 |

* Minimum and maximum values.

1) Mazout burned in firebox; 2) samples taken from; 3) composition of components in deposits; 4) moisture; 5) ash; 6) insoluble oxides; 7) organic part; 8) sulfurous cracking mazout; 9) screened* tubes; 10) convective tubes; 11) steam superheater; 12) none; 13) same; 14) traces; 15) straight-run sulfurous mazout; 16) low-sulfur mazout.

surfaces. The latter is due to the hygroscopicity of certain salts and the microporosity of the deposits, which cause capillary condensation of moisture. It has been further established that when sulfurous mazouts are burned, the deposits form more rapidly than in combustion of low-sulfur mazouts. In this case, we apparently have a manifestation of the vanadium effect, which contributes, as noted earlier, to deposit formation. As a result, the matter of timely removal of deposits from boiler heating surfaces when sulfurous mazouts are used acquires particular importance.

When high-viscosity mazouts in which there is an elevated content of ash are burned, the ash deposits are particularly destructive, since they stick to the boiler surfaces in an extremely tough crust that is practically immune to removal with an ordinary soot blower.

Steam cleaning or air-blast cleaning, water rinsing and mechanical cleaning (scrapers, brushes, etc.) are applied to remove the deposits. When steam is used, the structure of the deposits on subsequent heating surfaces deteriorates and intensified corrosion is possible, particularly when sulfurous fuels are burned [12], so that it is advisable to replace the steam with dry air.

Since blasting the boiler heating surfaces is of little effect when high-sulfur mazouts are burned due to the dense structure of the deposits, and mechanical cleaning is an extremely laborious and time-consuming operation, other countermeasures against the deposits have recently been coming into use. For example, shot blasting of the convective and tail-end heating surfaces is being employed abroad and in the USSR. Additives of various types are used on a much wider scale when mazouts are burned in boiler installations. The additives either raise the softening temperature and melting point of the ash-forming components or prevent adhesion of low-melting ash particles.

In the former case, the quantity of ash deposited is reduced, and in the latter, the additive improves the structure of the deposits, rendering them dry and friable, so that they can be removed easily by ordinary methods.

The structure of the deposits on the tail heating surfaces can be changed by the use of additives that react with $SO_3$. The additives not only change the structure of the deposits and reduce the quantity formed, but also inhibit corrosion of the heating surfaces. The additives used are slaked lime with a CaO content of 50-60%, dolomite (CaO – 30-34%, MgO – 21-22%, $CO_2$ – 38-48%), magnesite, alumina, kaolin, magnesium oxide, calcium oxide, ammonia and others.

Sulfur Content in Fuel

The content of sulfur in a mazout depends principally on the sulfur content in the crude petroleum in refining of which the mazout in question has been obtained. The greater the amount of sulfur in the initial petroleum, the more sulfur will there be in the mazout derived from this petroleum, with the sulfur content in the mazout being generally higher than that in the original petroleum.

Moreover, the quantity of sulfur in a mazout depends on the depth to which the light distillates have been removed from the petroleum and the degree of cracking. Sulfur content increases with increasing viscosity and density of the mazouts.

Knowledge of the total quantity of sulfur present in the fuel is necessary for thermal-engineering calculations and for estimating the corrosion processes that may take place under the influence of the sulfur's combustion products. It will be recalled that the maximum admissible sulfur content in fleet mazouts produced from sulfur-bearing petroleums is 2%, while that for firebox mazouts is 3.5%.

Usually, mazouts contain the so-called "volatile" sulfur, which

burns with the fuel; "sulfate" sulfur, which is present in the ash and does not participate in combustion of the fuel, is present in negligibly small quantities in mazouts.

Sulfur may be present in mazouts in the form of elementary sulfur, hydrogen sulfide, and various organic compounds (mercaptans, sulfides, disulfides, and the like). The most aggressive and toxic compounds (hydrogen sulfide, elementary sulfur and mercaptans) are present in mazouts in quantities considerably smaller than those observed in petroleum or in light distillates. Consequently, sulfurous mazouts are less toxic and less corrosively aggressive toward the mazout-handling equipment than the petroleum or the lighter products obtained in refining it.

Extensive operation with sulfurous mazouts has shown that they do not aggravate corrosion of the equipment (reservoirs, pipelines, pumps) as compared with low-sulfur mazouts.

Usually, irrespective of the origin of the mazout, the parts most liable to attack are the reservoir roofs (by vapors and gases) and those parts of metallic mazout storage tanks where the metal is in contact with water that has settled out of the mazout. The appearance of corrosion is hastened by warming and watering of the mazout. The corrosive aggressiveness of mazouts diminishes as their density and viscosity rise.

The total quantity of sulfur present in the mazout is of importance for the corrosion that takes place under attack by sulfur-combustion products, since all sulfur products produce sulfur oxides as a result of combustion, and the corrosiveness of these oxides depends on temperature, the dew point, and the presence of moisture. It is known that the smoke gases obtained on combustion of fuels may corrode the metal of the boiler apparatus only when the metal is very hot, at

a temperature at which reaction is possible between t' smoke gases and the metal or, on the other hand, so cold that condensation of combustion products begins.

Practical operation of boiler installations indicates that intensive heating-surface corrosion is observed in combustion of sulfurous fuels at points where the metal temperature makes it possible for the vapors present in the smoke gases to condense on it. The tail surfaces – the air preheaters, water economizers, and iron exhaust tubes – are most liable to this corrosion. In this case, electrochemical or sulfuric-acid corrosion takes place.

Fig. 183. $SO_3$ content in combustion products as a function of sulfur content in petroleum. 1) Firebox-wall temperature 1200°; 2) firebox-wall temperature 1600°. A) Volume content of $SO_3$ in combustion products, %; B) sulfur content in petroleum, %.

As we know, the sulfur burns to $SO_2$ during combustion of sulfurous fuels, although $SO_3$ is also detected in the combustion products. The conversion of $SO_2$ into $SO_3$ in combustion of mazouts amounts, according to literature data, to 3.2 to 7.4% for small fireboxes [37], and to 0.5 to 4.0% for large ones. According to certain sources [40], less than 5% of the total sulfur in the fuel is converted to $SO_3$, and the content of $SO_3$ in the exhaust gases (by volume) may drop to 0.005% in combustion of sulfurous mazouts. The formation of $SO_3$ is a function of the sulfur content in the fuel, the combustion temperature, and the excess-air ratio. A number of papers make reference to the fact that the formation of $SO_3$ also depends on the catalytic action of sulfates, ferric oxide and vanadium. The formation of $SO_3$ as a function of sulfur content and temperature is shown in Fig. 183. Grumley and Fletcher [37] es-

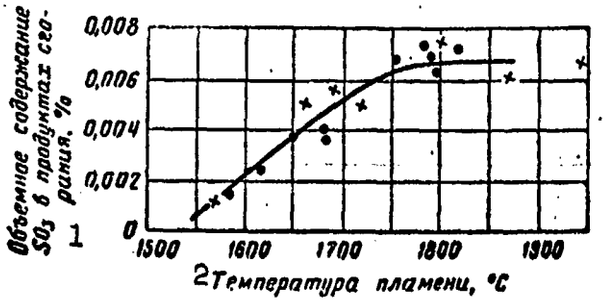


Fig. 184. $SO_3$ content in gases (12% $CO_2$) as a function of flame temperature. o) kerosene, 2% sulfur (disulfides); x) distilled petroleum, 3% sulfur. 1) Volume content of $SO_3$ in combustion products, %; 2) flame temperature, °C.

tablished that the $SO_3$ content first increases with increasing flame temperature and then approaches a constant value at flame temperatures above 1750° (Fig. 184). It is also shown in their work that the formation of $SO_3$ increases with increasing excess-air ratio. As the excess-air ratio is increased from 1.1 to 1.7, oxidation of $SO_2$ to $SO_3$ is doubled.

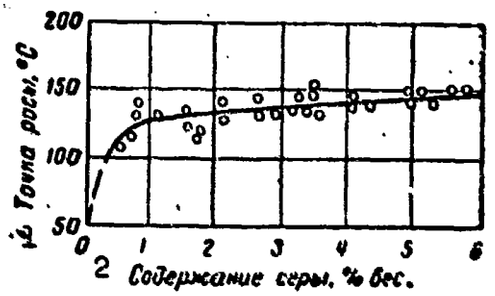


Fig. 185. Dew point as a function of sulfur content. 1) Dew point, °C; 2) sulfur content, % by weight.

The presence of even small quantities of $SO_3$ in the exhaust gases considerably increases the effective temperature of initial moisture condensation as against that corresponding to the partial pressure of pure water vapor in the combustion products.

The temperature at which condensation of the water vapors present in the gases is possible (dew point of exhaust gases) is the higher the higher the concentration of water vapor, and averages 45-65°.

When mazouts with high sulfur contents are burned, condensation of the vapors takes place at higher temperatures, which may reach 120-

150° [40], since in this case sulfuric-acid vapors which form when $SO_3$ reacts with water vapor are condensing.

Figure 185 shows the dew point of exhaust gases as a function of sulfur content according to [38]. At a 1% sulfur content in the fuel, the exhaust-gas dew point rises to 130°. With sulfur contents from 1 to 5%, each percentage-point increase raises the dew point by about 4° [38]. According to the VTI [39], the dew points of mazouts are lower than stated in [38] by about 10°.

Since the temperature of the boiler tail surfaces (air preheaters, economizers) is identical to or lower than the exhaust-gas dew point of sulfurous mazouts, it is on these surfaces that most of the sulfuric acid condenses. It was indicated earlier that the boiler heating surfaces are covered with ash deposits, so that on condensation the acid gets into the deposits and is present in them in the form of free sulfuric acid, which penetrates to the surface of the metal and intensifies corrosion of it.

Table 140 presents the author's data on the free-sulfuric-acid content in deposits taken from the economizers and convective-tube bundles of boilers operated on sulfurous and low-sulfur mazouts. The free sulfuric acid was determined by the method developed by Yu.M. Kostrikin and V.A. Rumyantseva.

In deposits taken from the lower rows of tubes, where the wall temperature is 110-115°, the free sulfuric acid content was highest. Moreover, an elevated content of free sulfuric acid in the deposits also corresponds to a larger sulfur content in the mazouts. The corrosion rate under attack by sulfuric acid depends on the acid concentration, which, in turn, depends on the wall temperature (Figs. 186 and 187) [41].

Corrosion is insignificant when sulfurous mazouts are burned at

TABLE 140

Free Sulfuric Acid Content in Deposits (in %)

| 1 Место отбора проб отложений | Содержание свободной $H_2SO_4$, % 2 | |
|---|---|---|
| | 3 мазут ФС-5 (S = 1,8%) | мазут Ф-12, 4 (S = 0,8%) |
| 5 С нижних рядов труб экономайзера | 5,36 | 1,22 |
| 6 С верхних рядов труб экономайзера (у газохода) | 70,81 | 7 Отсутствует |
| 8 С труб конвективного пучка | Отсутствует | » |

1) Point at which deposit samples taken; 2) content of free $H_2SO_4$, %; 3) FS-5 mazout; 4) F-12 mazout; 5) from lower rows of economizer tubes; 6) from upper rows of economizer tubes (at flue); 7) none; 8) from convective-bundle tubes.

wall temperatures of 65-105°, but at temperatures from 110° to the dew point of sulfuric acid, as well as below 65°, corrosion intensifies [42].

Protection of the tail-end heating surfaces from corrosion is one of the most important problems in boiler design, since low-temperature corrosion of air preheaters and economizers may be so severe that they

Fig. 186. Corrosion rate of steel (C – 0.15%) as a function of temperature with constant $H_2SO_4$ concentration. 1) $H_2SO_4$ concentration 65%; 2) $H_2SO_4$ concentration 95%. A) Temperature, °C; B) corrosion rate, g/m²·hour.

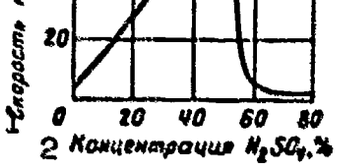


Fig. 187. Corrosion rate of carbon steel (C – 0.19%) as a function of $H_2SO_4$ concentration at constant temperature. 1) corrosion rate, g/m²·hour; 2) $H_2SO_4$ concentration, %.

TABLE 141

Composition of Steels (in %)

| 1 Материалы | C | Mn | Cr | Ni | Cu | Fe | 2 Прочие |
|---|---|---|---|---|---|---|---|
| 3 Инконель | 0,08 | 0,25 | 14 | 78,70 | — | 6,50 | — |
| 4 Карпентер 20 | 0,07 | 0,75 | 20 | 29 | 3 | 44,20 | 2 |
| 5 Сталь 304 | 0,05 | 1,50 | 19 | 10 | — | 68 | — |
| 6 Сталь 310 | 0,20 | 1,50 | 25 | 20 | — | 52 | — |
| 7 Картен | 0,10 | 0,40 | 0,90 | 0,45 | 0,40 | 97,00 | — |

1) Material; 2) other; 3) Inconel; 4) Carpenter 20; 5) steel 304; 6) steel 310; 7) Carten.

are quickly rendered useless. The following countermeasures are taken against low-temperature corrosion: protection of the metallic heating surfaces with acid-resistant coatings, the use of materials that have relatively high corrosion resistance, raising the heating-surface temperature of the dew point, and reducing $SO_3$ formation by the use of additives.

Protection of the heating surfaces by raising the wall temperature usually results in an increased flue-gas temperature and a considerable drop in the efficiency of the boiler installations. Selection of corrosion-resistant steels for the tail-end heating surfaces has shown that the corrosion rate may take a maximum and a minimum for each metal at certain acid concentrations. In view of the fact that the temperature of the tail-end heating surfaces varies over a wide range and, consequently, that the acid may have different concentrations, selection of the proper material is a very difficult matter. According to [43], the highly alloyed Inconel and Carpenter 20 have low corrosion rates. Also recommended [44] are steel 304 and steel 310. Among the inexpensive low-alloy steels, Carten steel has been suggested; this contains up to 97% of iron and small additives of Mn, Cr, Ni, and Cu. This steel has good corrosion resistance in the acid-concentration range from 40 to 90%, i.e., under conditions simi-

lar to those prevailing. The compositions of the steels are listed in Table 141.

Encouraging results were obtained when various types of enamels [40, 45] were used to protect the heating surfaces. Among others recommended for these purposes is acid-resistant enamel 105, which is particularly resistant to $H_2SO_4$ concentrations from 50 to 90%.

The tail heating surfaces may be protected from corrosion by the use of additives that reduce the content of $SO_3$ in the combustion products and depress the dew point. Additives that adsorb $SO_3$ have been tested for this purpose; examples are dolomite and silica in quantities of 0.1-0.2% of the weight of the fuel. These additives reduce corrosion markedly, but depress the dew point only insignificantly. The drop in corrosion is accounted for by the considerable increase in the quantity of deposits formed on the heating surface and by changes in their structure. Better results were obtained by injecting additives that enter into chemical reaction with $SO_3$ – compounds of zinc, magnesium and ammonia. These additives depress the dew point of the smoke gases and inhibit corrosion significantly.

When ammonia is injected into the firebox at a temperature of 300° in concentrations above 0.021% by weight, the dew point of pure water vapor is reached. Figures 188 and 189 show curves of dew point as a function of ammonia concentration and a curve of corrosion rate as a function of temperature, with and without ammonia [38].

Table 142 lists the minimum additive concentrations required in the fuel to lower the smoke-gas dew point to that of water vapor, according to [38]; these data were obtained in test-stand experiments with a fuel containing 3.2-3.4% sulfur.

To prevent sulfuric-acid corrosion with wall temperatures below the dew point, one English firm has patented (British patent 734190)

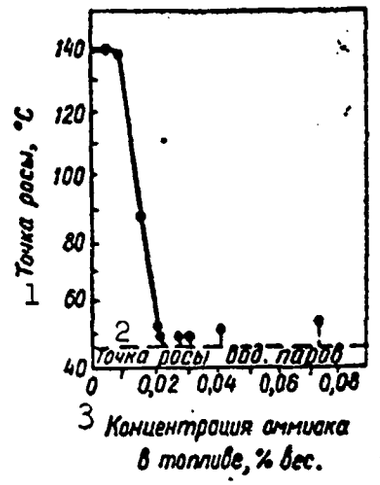


Fig. 188. Variation of dew point as a function of ammonia concentration. 1) Dew point, °C; 2) dew point of water vapor; 3) ammonia concentration in fuel, % by weight.

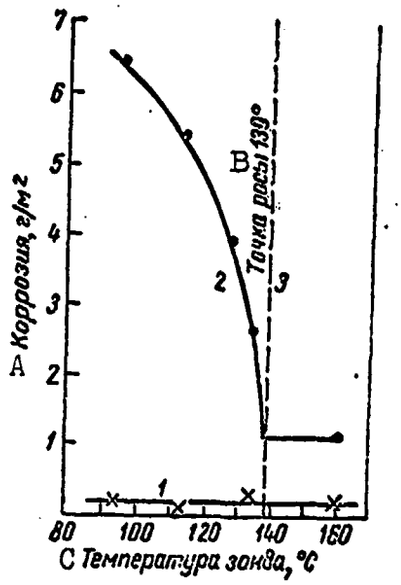


Fig. 189. Effect of ammonia injection on corrosion. 1) With injection of ammonia; 2) without ammonia; 3) dew point 139° (without ammonia). A) corrosion, g/m$^2$; B) dew point 139°; C) probe temperature, °C.

the additive "Teramine" (trademark of apparatus [sic]) [46]. Teramine is one of the tertiary heterocyclic amines produced from coal tar. Teramine is introduced into the boiler flues at a point where the gas temperature is about 250°, in the atomized state and in quantities equal to 0.03-0.05% of the weight of fuel consumed. Due to the lowering of the flue-gas temperature when Teramine is used, the efficiency of the boilers was raised by 1.5% in addition to the reduced corrosion of the tail-end surfaces.

In summarizing the above, it must be acknowledged that the most effective countermeasure against tail-surface corrosion is the use of additives.

Experimental studies must be carried out to further extensive introduction of these techniques and selection of the proper additives.

TABLE 142

Minimum Additive Concentrations Required to Depress Dew Point of Smoke Gases to Dew Point of Water Vapor and Their Cost

| 1 Присадка | 2 Метод ввода присадки | 3 Минимальная концентрация в топливе, % вес. | 4 Стоимость присадки на 1 т топлива, руб.* |
|---|---|---|---|
| 5 Аммиак | 6 Вдувается в дымовые газы при температуре 350° | 0,06 | 0,6 |
| 7 Цинковая пыль | 8 Добавляется в топливо в виде суспензии . . . . | 0,47 | 6,1 |
| 9 Доломит | 10 То же . . . . . | 0,80 (Ca + Mg) | 9,7 |
| 11 Окись магния | » | 0,35 (Mg) | 16,1 |
| 12 Нафтенат цинка | 13 Добавляется к топливу в виде раствора . . . . | 0,22 (Zn) | 53,5 |
| 14 Нафтенат магния | То же . . . . . | 0,15 (Mg) | 81,5 |

* Based on American prices.

1) Additive; 2) method of injecting additive; 3) minimum concentration in fuel, % by weight; 4) cost of additive per 1 ton of fuel, rubles*; 5) ammonia; 6) blown into smoke gases at temperature of 350°; 7) zinc dust; 8) added to fuel in form of suspension; 9) dolomite; 10) same; 11) magnesium oxide; 12) zinc naphthenate; 13) added to fuel in solution form; 14) magnesium naphthenate.

The elevated sulfur content in high-sulfur mazouts provides a basis for assuming that their toxic activities will be higher as compared with low-sulfur mazouts. It is known that the volatile compounds evolved from sulfurous and low-sulfur mazouts have a toxic effect on the human organism, particularly at elevated temperature and irrespective of sulfur content.

The toxicity of sulfurous mazouts is higher basically because of the hydrogen-sulfide and mercaptan content and, on combustion, because of the $SO_2$ that is formed. Hydrogen sulfide is deadly in a concentration of 1 mg/liter.

During storage and shipment of sulfurous mazout, the hydrogen sulfide content present may change; on heating, the sulfur compounds may decompose with evolution of hydrogen sulfide [27].

Precautionary measures must be taken in work with sulfurous

mazouts; these include hermetic sealing for tank cars and pipelines, prevention of smoke gases from the flues entering work and residential premises, and the installation of sufficiently powerful ventilation facilities.

These requirements must be observed carefully where sulfurous mazouts are used on seagoing and river vessels, where the proximity of the fuel tanks to living quarters increases the danger that the sulfurous mazouts will have harmful effects on personnel.

It is recommended that high-viscosity sulfurous mazouts (viscosities above $VU_{50}$ = 12) with open-crucible flash points of about 100° be burned in the fireboxes of ship boilers; these should be less toxic than low-viscosity mazouts, since they contain much smaller quantities of light petroleum distillates.

Extensive operating experience of oceangoing vessels and tugboats and river passenger vessels has shown that burning sulfurous mazouts in the steam-boiler fireboxes does not give rise to further expected [sic] complications.

At the present time, the refining industry is producing the following grades of liquid boiler fuel: 1) fleet mazout; 2) petroleum fuel (mazout); 3) Ukhta boiler fuel; 4) coal-and-shale fuel mazout (shale oil).

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[List of Transliterated Symbols]

| | |
|---|---|
| 594 | р = r = rabochiy = working |
| 594 | с = s = sukhiy = dry |
| 594 | г = g = goryuchaya = combustible |
| 594 | л = l = letuchiy = volatile |
| 595 | н = n = nizshiy = lower |
| 596 | Э = E = Ekvivalent = Equivalent |
| 596 | кал = kal = kaloriynyy = calorific |
| 596 | пол = pol = poleznyy = useful |
| 596 | усл = usl = uslovnyy = conventional |

## Chapter 20

## FUELS FOR AIR-REACTION ENGINES

Aircraft with air-reaction engines occupy the leading position in present-day military and civil aviation. Air-reaction engines (VRD) have come to replace piston engines in aviation. This is connected with the fact that, as Fig. 190 shows, they are considerably better than piston engines with respect to their flight and operating possibilities. Actually, with the utilization of VRD in aviation, the recent past has seen flight speeds at the speed of sound, and then 2-2.5 times the speed of sound; with the utilization of VRD, there has also been a considerable increase in the flight altitude of modern aircraft.

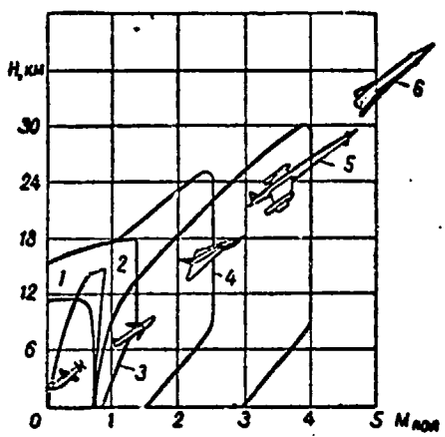


Fig. 190. Regions in which it is desirable to use flying craft with piston (1), turboprop (2), turbojet (3), turbojet with afterburner (4), ramjet (5), and rocket (6) engines.

Our country takes a leading role in the development of air-reaction engine aviation. By the middle of the nineteenth century, the Russian engineers and inventors I.M. Tretesskiy, N.M. Sokovnin, and N.A. Teleshev had proposed designs for engines including the basic elements of modern VRD. In 1897, the engineer P.D. Kuz'minskiy constructed the first gasturbine engine, using kerosene as the fuel; at the present time, this material is widely used as a fuel for VRD. During the 1906-1908 period, engineer Korovodin built a gasoline-operated pulsejet engine. In 1911, engineer Gorokhov proposed a

motor-compressor VRD, also using petroleum fuel.

The development of jet engineering in the USSR is inseparably associated with the name of a great Russian scientist, the father of Russian aviation, N.Ye. Zhukovskiy, who as early as the 1882-1886 period had developed for the first time the main topics in the theory of jet motion, and also with the name of the prominent Russian inventor and scientific innovator K.E. Tsiolkovskiy, who together with noteworthy designs for jet aircraft developed in 1932 developed a double-flow air-reaction engine with compressor and propeller driven by a piston engine.

The theoretical studies of B.S. Stechkin [1] were a major contribution to the development of air-reaction engines, as were the experimental investigations and pilot design work of the Soviet designer A.N. Tupolev, V.V. Il'yushin, and others.

Owing to this work, Soviet air-reaction aviation presently leads the world. Soviet aircraft with turbojet and turboprop engines, the TU-104, TU-104B, TU-114, AN-10, and Il-18 have won wide recognition both here in our country and abroad. Soviet aircraft with air-reaction engines have established world records for speed, range, and altitude.

Of great importance in the development of air-reaction engines has been the work of Soviet scientific-research and experimental institutions in the field of fuels for these engines [2-23].

The T-1 and TS-1 high-performance fuels, obtained by Soviet petroleum organizations during the 1946-1954 period have facilitated the success of our air-reaction aircraft.

The work of foreign scientists [24-29] has also been of great importance to the development of fuels for VRD.

CONDITIONS UNDER WHICH FUELS ARE USED IN VRD

The operation of air-reaction engines, both compressorless and

compressor-type, is based upon the creation of a powerful gas-air stream within the engine, capable of turning engine components at high speeds, and of creating considerable reaction thrust upon leaving the engine, thus providing high-speed flight for modern aircraft. The gas-air stream in a VRD is formed in combustion chambers in which fuel is burnt in a stream of air (see Chapter 6). In compressorless engines, the air arrives at the combustion chamber under ram pressure, while in compressor types, a powerful centrifugal or axial air compressor is used.

The simplest compressorless VRD is the ramjet engine PVRD [30], a diagram of which has been given previously (see Fig. 45 in Chapter 6). Air is compressed in the diffuser owing to its kinetic energy; thus the ramjet can operate only in a stream of air. The oncoming air stream enters an expansion diffuser, and loses a portion of its speed. This raises its pressure, density, and temperature in accordance with the initial velocity of the stream. In the front section of the combustion chamber, the air is mixed with the fuel, which is injected through a nozzle in fixed proportion to the amount of air. The fuel vaporizes, forming a combustible mixture that continuously feeds the combustion zone established in the central portion of the combustion chamber beyond the flameholder. From the combustion chamber, the gases go to the exhaust nozzle, where their velocity increases; it will be greater than the velocity of the incoming stream. Owing to the great acceleration of the gases, jet thrust will appear and act upon the engine.

At the present time there are two types of PVRD: subsonic and supersonic (SPVRD). The distinguishing feature of the SPVRD is the higher temperature and pressure of the air arriving in the combustion chamber and of the gases formed in it.

The engine most commonly encountered in present-day aviation is

the turbocompressor air-reaction engine (TRD). There are straight and double-flow TRD, as well as combinations of TRD with propellers – turboprop engines (TVD).

A modern turbocompressor VRD consists of the following elements: inlet diffuser 1, axial compressor 2, combustion chamber 3, gas turbine 4, exit diffuser 5, afterburner 8, and jet nozzle 9. The arrangement of a modern TRD with afterburner, and the change in gas characteristics along its length are shown in Fig. 191 [31]. The engine operates in the following manner. Air, passing through the inlet diffuser, is sent to the compressor where its pressure is increased by 3.5-4.5 times as a result of compression. The air at elevated pressure is directed into the combustion chamber, where fuel is injected through a nozzle. The formation of a fuel-air mixture and its combustion occurs in the combustion chamber; here the gas temperature is increased to 1400-1550°.

An additional quantity of air is supplied to a secondary zone of the combustion chamber in order to drop the gas temperature and to ensure complete combustion of the fuel. If the fuel-air ratio in the primary combustion-chamber zone approaches unity, 4 times as much air is supplied to the secondary zone as to the primary.

From the combustion chamber, gas at a temperature of 650-700° is sent to the gas turbine, setting it in motion. A certain amount of the energy of the gas is used to turn the turbine and the compressor connected to it; this causes a partial drop in temperature and pressure. Next, the gas goes through a diffuser to the afterburner, where additional fuel is injected through nozzle 6. Beyond the special flameholder 7, which maintains the flame, steady combustion occurs, creating at the nozzle exit a high-temperature and high-speed stream. Consequently, a modern TRD in essence represents a combination of a tur-

bocompressor and ramjet engine.

The turboprop engine (TVD) and double-flow engine (DTRD) are varieties of TRD.

The operation of the TVD, a diagram of which is given in Fig. 44

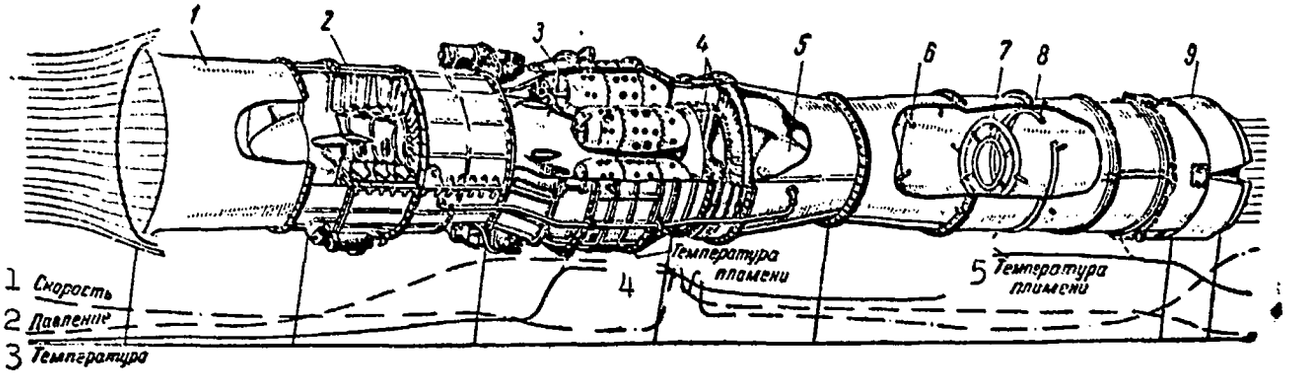


Fig. 191. Arrangement and change in gas-stream parameters in TRD with afterburner. 1) Velocity; 2) pressure; 3) temperature; 4) flame temperature; 5) flame temperature.

of Chapter 6 [32] is based upon the utilization of the excess energy created by a gas turbine [32] for driving a propeller. Since the compressor absorbs most of the power and the jet thrust is thus very small, the basic thrust of such an engine is created by the propeller. Turboprop engines create considerably more thrust at low flight speeds and especially at takeoff than do TRD. TVD are employed for flight speeds of up to 600-800 km/hr. The fuel consumption of a TVD is about 0.35-0.40 kg/hp-hr. The same kerosene-type fuel is used for TVD as is used for TRD. Specific specifications for TVD fuel have not as yet been established.

In double-flow TRD, the excess power is transmitted not only to a propeller, but also to a fan that forces the air through a separate circular duct, forming an external engine system. The arrangement and operation of the internal system differs in no way from the operation of an ordinary TRD. The external system works in the following manner. The air entering the external system passes through a diffuser to the

fan. The fan creates a small pressure rise in the second system, and moves large masses of air which then are sent into the jet nozzle. Here the energy obtained by the air in the fan is converted into kinetic energy, thus raising the velocity of the gases, and producing jet thrust. At flight speeds of up to 600-700 km/hr, DTRD develop greater thrust than TRD. The specific fuel consumption in a DTRD is considerably lower under these conditions than in a TRD, and reaches 0.65 kg/kg-hr. A DTRD normally operates with the same fuels used by straight engines.

VRD belong to the class of engines with continuous fuel injection. In contrast to piston engines with continuous injection, VRD are characterized by uninterrupted supply of fuel and air to the combustion chamber. An exception is the pulsejet engine [Pu VRD], in which the fuel, as in piston engines, is injected intermittently. At present, the pulsejet is not widely used. It was only during the Second World War in Germany that the pulsejet was used in certain flying craft – the "V-1" missiles. Automotive gasoline was used as the fuel for these engines.

Fuel is supplied to the combustion chambers of VRD with the aid of a fuel system, whose basic arrangement is shown in Fig. 192 [5]. While fuel is pumped through the fuel system, it comes into contact with numerous parts of the fuel units, which are made of various ferrous and nonferrous alloys. Thus, the fuel-collector ducts, fuel-filter rings, rings and screens of the filters in the working and starting nozzles are made of brass, the fuel-pump rotor is bronze, the fuel-pump housing and fuel accumulator are made from an aluminum alloy, etc. In some systems, individual parts of fuel units may be plated with nonferrous metals. Thus, the springs and cup of fuel-pump screen filters are cadmium plated; the ends of the fuel-pump rotor are lead-indium

plated, etc. [33, 34].

Despite the high speed at which the fuel is pumped, nonferrous metal alloys have a negative effect upon fuel quality. This applies primarily to copper alloys, and especially to types VB-24 and VB-23NTs bronzes, from which fuel-pump rotors are made. When these alloys are present in the fuel, solid insoluble sediments form, clogging the fuel filters and causing precision mated elements of fuel units to seize. The formation of deposits in the fuel in the presence of copper alloys is intensified at the elevated fuel temperatures that may occur in modern engines.

The fuel may become quite hot in supersonic aircraft. At greater-than-sound flight speeds, the fuel in the tanks is heated owing to the heat produced by friction of the air on the aircraft body. In addi-

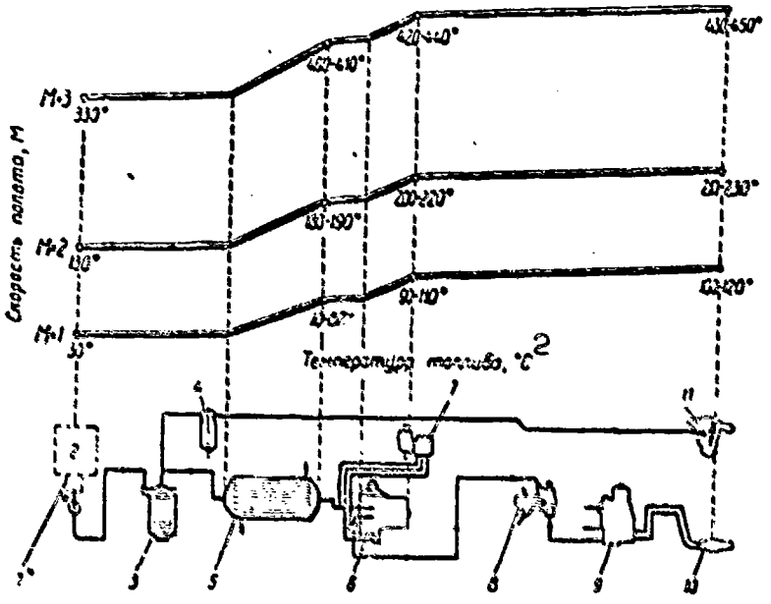


Fig. 192. Basic arrangement of TRD fuel system and change in temperature throughout its length as a function of aircraft flight speed. 1) Booster pump; 2) fuel tank; 3) filter; 4) starting pump; 5) fuel-oil radiator; 6) pump; 7) barostat; 8) throttle valve; 9) distributor; 10) nozzle; 11) starter.

tion, in a VRD, the fuel may become heated in the fuel pumps and in

the fuel-oil radiators. In absorbing heat from the pumps, which rotate at high speed, the fuel may be heated by an additional 20-30°. In the fuel-oil radiators, the fuel is used to cool the oil, which is at a temperature of 130-250° or above; this will produce a further temperature rise in the fuel of 30-40°. Finally, the fuel system, as a rule, is installed on the air-compressor housing; the temperature of the last stages of this unit reach 200-250°, which also causes some additional heating of the fuel. Figure 192 shows the change in fuel temperature, based upon calculated data, as it passes through the elements of the fuel system, as a function of increasing aircraft flight speed. It follows from the data given that at a flight speed of Mach 1, the maximum fuel temperature may reach 100-120°, at Mach 2 – 210-230°, and at Mach 3 – 430-450°. At such temperatures, not only will solid sediments be formed in the fuel, but it will in turn prove to be heavily corrosive with respect to the parts of fuel units made of nonferrous alloys.

Fuel heating is characteristic not only of supersonic aircraft, but of subsonic craft as well. Owing to the use of fuel as a cooling agent in several elements of the fuel system in a subsonic jet aircraft, the fuel temperature may reach 80-110°.

SPECIFICATIONS FOR TRD FUEL

The basic TRD units that have a substantial influence upon fuel specifications are the combustion chamber, fuel system, and gas turbine. Accordingly, we shall consider the arrangement and operation of these units, as well as the specifications imposed upon the fuel from the viewpoint of normal operation of these units. Figure 193 shows schematically a TRD, and indicates the basic fuel characteristics that affect the operation of the individual motor units [35].

The fuel system of a TRD is one of the principal parts of the

gine. A change in engine operating conditions is carried out by changing the quality of the fuel supplied to the combustion chamber. Thus

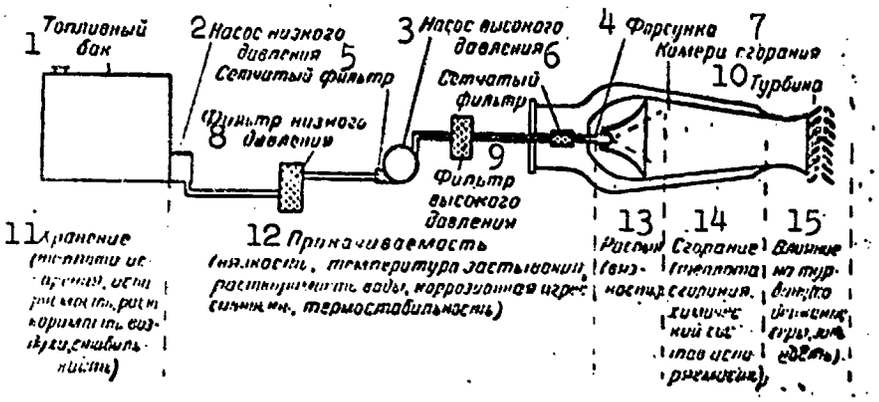


Fig. 193. Fuel characteristics required by various TRD units. 1) Fuel tank; 2) low-pressure pump; 3) high-pressure pump; 4) nozzle; 5) screen filter; 6) screen filter; 7) combustion chamber; 8) low-pressure filter; 9) high-pressure filter; 10) turbine; 11) storage (heat of vaporization, volatility, solubility of air, stability); 12) pumpability (viscosity, freezing point, solubility of water, corrosive aggressiveness, thermal stability); 13) atomization characteristics (viscosity); 14) combustion (heat of combustion, chemical composition, volatility); 15) effect upon turbine (sulfur content, ash).

uninterrupted operation of the fuel system is of primary importance. The basic fuel system of a TRD consists of the following elements: fuel tanks, fuel booster pumps, low-pressure fuel filter, fuel-oil radiator, fuel pump regulator, piping, and nozzles. As a rule, a screen or paper high-purification filter is located before the pump regulator. High-purification filters are also installed before the fuel regulators.

The engine fuel system works as follows. Fuel from the fuel tanks is pumped through the fuel filters and the oil-fuel radiator by electric pumps to the pump regulator, and then, after passing through a series of fuel regulators, it is sent to the combustion-chamber nozzles.

A characteristic feature of modern VRD fuel systems is the pre-

sence of finely adjusted fuel apparatus, having numerous precision mating elements with small clearances. In order to guarantee reliable operation of this apparatus, several high-purification filtering elements are installed in the fuel system, having mesh spacings of from 5 to 120 microns.

The basic requirement for fuel, related to reliable fuel-system operation is uninterrupted pumpability under various operating conditions, especially at low temperatures (about -50, -60°), and at high temperatures (about 120-200°). To satisfy this requirement, the fuel should having the following properties.

1) it should not freeze and it should not precipitate crystals of high-freezing hydrocarbons at low temperature (down to -50-60°);

2) it should not develop ice crystals, and they should not clog the fuel filters;

3) it should not liberate vapors of low-boiling components, nor should it form vapor locks in the fuel system;

4) at temperatures of 120-200°, it should not form solid insoluble sediments, and they should not clog the fuel filters;

5) gum deposits should not be formed on parts of the fuel apparatus (valves or regulators);

6) it should not cause corrosion of fuel-system units, nor should it form corrosive deposits or clog the fuel units with corrosion products.

Combustion chambers of modern VRD are of the ramjet type. In them, combustion takes place continuously at high temperatures, which facilitates rapid accomplishment of the chemical reaction between the fuel and oxygen of the air after they are mixed. The rate of combustion in VRD is determined by the mixture-formation process. High-grade mixture formation is achieved by increasing the uniformity of the fu-

of atomized fuel, by fine dispersion and agitation of the stream in the combustion zone. Fuel quality has a substantial influence upon this process.

As altitude increases, there is a drop in the temperature and pressure of the air reaching the chamber. Under cruising conditions, the combustible mixture becomes lean. This decreases combustion stability down to the point at which the jet is interrupted and flameout occurs. As a rule, it is difficult to reignite the mixture under these conditions.

In order to provide reliable combustion-chamber operation, the fuel must:

1) be dispersed satisfactorily under various engine operating conditions, especially at low speeds;

2) provide reliable operation of the combustion chamber over a broad range of cooling-air parameter variations, as well as for various excess-air ratios;

3) ignite when the engine is started, for various characteristics of the air entering the chamber;

4) provide very complete combustion of the fuel;

5) provide a combustion rate such that the combustion process is completely finished in the combustion chamber, i.e., produce the smallest possible combustion zone.

The fuel should not:

1) produce carbon deposits in the combustion chamber or on other engine parts, leading to warping of the combustion-chamber walls and to failure;

2) form combustion products having a harmful effect upon the combustion-chamber walls, upon the turbine blades, or the exhaust nozzle.

In order to provide reliable gas-turbine operation, the fuel

should have a minimum content of ash, which erodes the turbine blades, and also fouls the blade locks, resulting in blade failure.

Several requirements originate in the operating and working peculiarities of modern jet aircraft using VRD. Modern jet aircraft have a very limited fuel-storage volume. The climb rate of jet aircraft is very high, so that in climbing to an altitude of 15-18 km, the fuel in a tank cannot cool, but remains at the ground temperature. Moreover, in supersonic aircraft, the fuel temperature in the fuel tanks may rise owing to aerodynamic heating to 120-250°. In accordance with these peculiarities, following fuel specifications are necessary:

1) it should possess maximum energy characteristics;

2) it should not boil or foam in the fuel tanks, so that it will not transport any air in solution, and it should contain no low boiling components;

3) it should have high thermal stability, i.e., it should not form solid insoluble sediments in the fuel tanks.

Finally, for reliable fuel storage in fuel warehouses, it should resist oxidation by the oxygen of surrounding air.

GRADES OF FUELS FOR VRD

Modern thermal-jet engines use various fuels. There are two groups of fuels for VRD: mineral fuels of hydrocarbon composition, and nonhydrocarbon chemical fuels. Mineral fuels are obtained chiefly from petroleum, as well as from products obtained by processing solid minerals. At the present time, petroleum fuels for VRD are very common. They are classified according to method of production into straight-distillation fuels and fuels obtained by secondary processes: thermal and catalytic cracking, polymerization, etc. Mineral fuels for VRD are classified according to fraction composition into fuels of the gasoline type, the naphtha type, the kerosene type, the gas-oil type,

the wide-boiling type. At the present time, the most common fuel types are kerosene and the wide-boiling type, both of which are obtained by straight distillation. Attempts to use products of thermal or catalytic cracking as fuels for VRD has as yet not yielded positive results. This is due to the inadequate stability of these fuels upon heating to which the fuel may be subjected in the engine fuel system. The question is also considerably complicated by the continuous temperature rise in the fuel systems of modern supersonic aircraft.

Studies on the utilization of gas-oil type fuels for VRD have also been unsuccessful. Gas-oil type fuel tests carried out during the 1945-1949 period under bench and flight conditions showed that these fuels have many substantial drawbacks, especially in respect to providing combustion stability, restarting in flight at high altitudes, and with regard to the low-temperature properties. An important negative feature of these fuels is the fact that they are not produced in adequate quantities, since their output amounts to no more than 10-15% of petroleum production.

Kerosene-type fuel is considered to be the best fuel for VRD in respect to operating characteristics. It has a low crystallization point, low vapor pressure, and is relatively fire resistant; it has the best energy characteristic.

Wide-boiling type fuels appeared in the 1949-1953 period. The basic factor for the appearance of these fuels is the attempt to expand fuel resources for VRD by using the gasoline, naphtha, kerosene, and, in part, the gas-oil fractions of petroleum. Flight tests of these fuels have shown that the inclusion of large quantities of the gasoline fraction in their composition is undesirable owing to the extremely high volatility of the fuel in high-altitude flights, and its poor wear-resistant properties. In this connection, the content of

gasoline fractions in these fuels is presently limited so that the fuel vapor tension does not exceed 100-150 mm Hg, and the fuel viscosity at 20° does not drop below 1 centistoke.

Below we give characteristics of fuels used for VRD in other countries.

Domestic VRD fuels. In our country, four grades of fuel are presently used for VRD; they are produced by straight distillation of petroleum crude. The technical specifications for domestic VRD fuels are given in Table 143 [2, 3].

T-1 and T-5 fuels are of the kerosene type, TS-1 is of the heavy naphtha type, and T-2, of the wide-boiling type. T-1 and T-5 fuels are obtained from low-sulfur petroleums, fuel TS-1 and T-2 from sulfurous petroleums. Accordingly, the sulfur content in TS-1 and T-2 fuels may reach 0.25%. T-5 fuel differs from T-1 fuel in its greater density, greater content of heavy fractions, and relatively good refining.

T-1, T-5, TS-1, and T-2 fuels possess good operating characteristics, providing reliable operation of VRD. They are straight-distillation products, are highly stable, and may be stored under warehouse conditions for several years.

VRD fuels in the United States. The characteristics of fuels for VRD in the United States are given in Tables 144 and 145. At the present time, five grades of fuel are used for VRD in the United States, three of which (JP-1, JP-5, and JP-6) are kerosene-type fuels, and two (JP-3 and JP-4) are wide-boiling fuels [36, 37].

Type JP-4 fuel is very commonly used in the United States. Previously, cracking components were included in JP-4 fuel such that the bromine number did not exceed 30. At present, the content of unsaturated hydrocarbons in JP-4 fuel has been severely limited. The brom-

number of present-day JP-4 fuel should not exceed 3. This is connected with the fact that in the United States, there is yet no complete solution to the problem of attaining high-stability fuels containing a considerable amount of unsaturated hydrocarbons. In JP-4 fuel, the unsaturated and sulfur compounds are almost completely hydrogenated with the aid of hydrorefining, with the cracking components. Such JP-4 fuel differs little from straight-distillation fuels in unsaturated-hydrocarbon content.

JP-1 fuel is used far less frequently, chiefly in TRD for subsonic aircraft of older design. One of the chief reasons why JP-1 fuel is not presently in wide use is the limited nature of the resources for its production. Thus, JP-1 fuel can be obtained from some petroleums in amounts of no more than 10-15%.

JP-3 fuel is used chiefly in naval aviation in the United States. The requirements for this type of fuel presently amount to 7.5% of the total jet-fuel requirements of the United States. The main reason that JP-3 fuel does not find wide application is its high volatility, especially in high-altitude flights. In vapor pressure (368 mm Hg), JP-3 fuel is close to the aviation gasolines. The high vapor pressure of JP-3 fuel is due to the fact that low-boiling gasoline fractions are included in its composition, owing to which the initial boiling point of this fuel is 66°.

JP-5 fuel is designed for supersonic aircraft. Large amounts of the gas-oil fraction are included in this fuel in order to increase the density and expand production potentials. But this considerably impairs the low-temperature properties of the fuel; thus, for example, the crystallization point may reach -40°. This impairment of the low temperature properties of JP-5 fuel is permitted since the fuel is heated on board a supersonic aircraft, which eliminates the danger of

TABLE 143

Technical Specifications for T-1, TS-1, T-2, and T-5 Fuels

| 1 Физико-химические показатели | Т-1 ГОСТ 4138-49 | ТС-1 ГОСТ 7149-54 | Т-2 ГОСТ 8410-57 | Т-5 ГОСТ 9145-59 |
|---|---|---|---|---|
| 2 Плотность $\rho_4^{20}$ не ниже | 0,80—0,85 | 0,775 | 0,755 | 0,845 |
| 3 Фракционный состав: | | | | |
| а) температура начала перегонки, °С | 20 Не выше 150 | | 21 Не ниже 60 | 22 Не ниже 195; до 200° не более 2% |
| b б) 10% перегоняется при температуре в °С не выше | 175 | 165 | 125 | Не выше 225° |
| c в) 50% то же | 225 | 195 | 195 | |
| d г) 90% » | 270 | 230 | 250 | |
| e д) 98% » | 280 | 250 | 280 | 315 |
| f е) остаток и потери в сумме в % не более | 2 | 3 | 2 | 2 |
| 4 Вязкость кинематическая, *сст*: | | | | 23 |
| а) при температуре 20° не менее | 1,5 | 1,25 | 1,05 | Не более 5 |
| b б) » » 0° не более | 4 | 2,5 | 2,0 | |
| c в) » » —40° » » | 16 | 8,0 | 6,0 | 60,0 |
| d г) » » —50° » » | 25 | — | — | |
| 5 Кислотность в *мг* КОН/100 *мл* топлива не более | 1,0 | 1,0 | 1,0 | 1,0 |
| 6 Температура вспышки в °С не ниже | 30 | 28 | — | — |
| 7 Температура кристаллизации в °С не выше | —60 | —60 | —60 | —60 |
| 8 Температура помутнения в °С не выше | —50 | —50 | —50 | — |
| 9 Йодное число в *г* йода на 100 *г* не более | 2 | 3,5 | 3,5 | 3,0 |
| 10 Содержание ароматических углеводородов в % не более | 25 | 22 | 22 | 22 |
| 11 Содержание фактических смол, *мг*/100 *мл*: | | | | |
| а) на месте производства топлива не более | 8 | 7 | 7 | 8 |
| b б) на месте потребления топлива не более | 11 | 10 | 10 | 11 |
| 12 Содержание серы в % не более | 0,1 | 0,25 | 0,25 | 0,10 |
| 13 В том числе меркаптановой серы в % не более | — | 0,01 | 0,01 | — |
| 14 Содержание водорастворимых кислот и щелочей | 24 Отсутствует | | | |
| 15 Теплота сгорания низшая в *ккал/кг* не менее | 10 250 | 10 250 | 10 250 | 10 250 |
| 16 Зольность в % не более | 0,005 | 0,005 | 0,005 | — |
| 17 Содержание механических примесей и воды | 24 Отсутствует | | | |
| 18 Испытание на медной пластинке | 25 Выдерживает | | | |
| 19 Давление насыщенных паров при 38° в *мм* рт. ст. не более | — | — | 100 | — |

1) Physical-chemical characteristics; 2) density $\rho_4^{20}$, no less than; 3) fraction composition: a) initial distillation point, °C; b) 10% evaporated at temperature, °C, no greater than; c) 50%, the same; d) 90%, the same; e) 98%, the same; f) residue and losses, together, %, no more than; 4) kinematic viscosity, centistokes: a) at temperature of 20°, no less than; b) at temperature of 0°, no more than; c) at temperature of -40°, no more than; d) at temperature of -50°, no more than; 5) acidity, mg KOH per 100 ml of fuel, no

[Key continued on next page]

[Key to Table 143 continued]: more than; 6) flash point, °C, no less than; 7) crystallization point, °C, no more than; 8) cloud point, °C, no more than; 9) iodine number, g of iodine per 100 g, no more than; 10) content of aromatic hydrocarbons, %, no more than; 11) existent gum, mg/100 ml: a) at point of fuel production, no more than; b) at point of fuel consumption, no more than; 12) sulfur content, %, no more than; 13) including mercaptan sulfur, %, no more than; 14) content of water-soluble acids and alkalies; 15) low heat of combustion, kcal/kg, no less than; 16) ash, %, no more than; 17) content of mechanical impurities and water; 18) copper-plate test; 19) saturated vapor pressure at 38°, mm Hg, no more than; 20) no more than; 21) no less than; 22) no less than 195; to 200°, no more than 2%, no more than 225°; 23) no more than 5; 24) none; 25) satisfactory.

TABLE 144

Characteristics of Wide-Boiling Type Fuels for TRD

| 1 Физико-химические показатели | 2 Технические нормы | | 3 Качество | | |
|---|---|---|---|---|---|
| | JP-3 MIL-F-5624D (США) | JP-4[5] MIL-F-5624D (США) DERD-2486 (Англия), Air 3407 (Франция) | JP-3 MIL-F-5624D (США) | JP-4 MIL-F-5624D (США) | DERD-2486 (Англия) |
| 6 Плотность $\rho_4^{20}$ | 0,722—0,797 | 0,736—0,821 | 0,788—0,797 | 0,754—0,760 | 0,751 |
| 7 Фракционный состав, °С: | | | | | |
| 8 10% не выше | — | 121 | 66 | 82—102 | 101 |
| 20% » » | 116 | 144 | — | — | 112 |
| 50% » » | 177 | 188 | 173 | 143—152 | 156 |
| 90% » » | 243 | 243 | 249 | 208—227 | 229 |
| 9 к. к. в °С не выше | 315 | 288 | 286 | — | 250 |
| 10 Вязкость кинематическая в сст при температуре —40° С | — | — | 3,36 | 2,91 | 2,95 |
| 11 Бромное число в г брома на 100 г не более | 5,0 | 5,0 | — | 0,96—1,40 | — |
| 12 Температура кристаллизации в °С не выше | —60 | —60 | 28 Ниже | —60 | —60 |
| 13 Содержание ароматических углеводородов в % не более | 25 | 25 | 25 | 10—14,2 | 15 |
| 14 Содержание серы в % не более | 0,4 | 0,4 | 0,35 | 0,06—0,22 | — |
| 15 Содержание меркаптановой серы в % не более | 0,005 | 0,001 | 0,00 | ,00 | — |
| 16 Содержание антиокислителя в мг/л не более | 24 | 24 | — | — | — |
| 17 Содержание дезактиватора металла в мг/л не более | 5,6 | 5,6 | — | — | — |
| 18 Содержание воды в мг/л не более | 1,0 | 1,0 | — | — | — |
| 18а непредельных углеводородов в % не более | 5,0 | 5,0 | — | 1,0 | — |
| 19 Температура вспышки, °С | — | — | —23 | —13 | —15 |
| 20 Теплотворная способность в ккал/кг не ниже | 10 270 | 10 220 | 10400—10270 | 10400—10420 | 10 300 |
| 21 Содержание фактических смол в мг/100 мл не более | 7 | 7 | 1,2 | 1—1,7 | 2. |

TABLE 144 (continued)

| | | | | | |
|---|---|---|---|---|---|
| 22 Содержание потенциальных смол после 16 час. окисления в мг/100 мл не более | 14 | 14 | 8,4 | 1,0—6,2 | — |
| 23 Упругость паров в мм рт. ст. в пределах | 260—380 | 100—150 | 368 | 134—160 | 150 |
| 25 Проба на медную пластинку | 24 выдерживает | | | | |
| 26 Кислотное число, мг КОН/г | 0,1 | 0,1 | — | 0,05 | 0,1 |
| 27 Термическая стабильность по методу CFR: | | | | | |
| а) перепад давления на фильтре при 149 и 204°С, за 5 час. в мм рт. ст. не более | — | 325 [5] | — | — | — |
| б) количество отложений в подогревателе в баллах не более | — | 3 [5] | — | — | — |

1) According to Swiss standards – grade 1, Italian – AM/C-142, Canadian – grade 3 – GR-22A; 2) the limitations "not above" and "not below" refer solely to technical standards; 3) in Switzerland, 2 mg/l are permitted; 4) in France and Switzerland, 10 mg/100 ml are permitted; 5) for the English fuel DERD-2486 and for the American fuel, the determination is carried out but there is no standard.

1) Physical-chemical characteristics; 2) technical specifications; 3) grade; 4) Great Britain; 5) France; 6) density, $\rho_4^{20}$; 7) fractional composition, °C; 8) 10%, no more than; 9) end point, °C, no more than; 10) kinematic viscosity, centistokes, at temperature of -40°C; 11) bromine number in g bromine per 100 g, no more than; 12) crystallization point, °C, no more than; 13) content of aromatic hydrocarbons, %, no more than; 14) sulfur content, %, no more than; 15) mercaptan sulfur content, %, no more than; 16) content of antioxidant, mg/l, no more than; 17) content of metal deactivator, mg/l, no more than; 18) water content, ml/l, no more than; 18A) content of unsaturated hydrocarbons, %, no more than; 19) flash point, °C; 20) heating value, kcal/kg, no less than; 21) extant gum, mg/100 ml, no more than; 22) potential gum, following 16 hr oxidation, mg/100 ml, no more than; 23) vapor pressure, mm Hg, within; 24) satisfactory; 25) copper-plate tests; 26) acid number, mg KOH/g; 27) thermal stability, CFR method: a) pressure drop at filter, 149 and 204°C, after 5 hr, mm Hg, no more than; b) amount of deposits in heater, arbitrary scale, no more than; 28) below.

TABLE 145

Characteristics of Kerosene-Type Fuels for TRD

| 1 Физико-химические показатели | 2 Технические нормы | | Качество | | | |
|---|---|---|---|---|---|---|
| | JP-4 MIL-F-5616C (США), DERD-2482 (Англия) Air 3405 (Франция) 3 4 5 | JP-5 MIL-F-5624D (США), DERD-2488 (Англия) 4 | JP-4 MIL-F-5616C | JP-5 MIL-F-5624D | DERD-2482 (Англия) 4 | DERD-2488 (Англия) 4 |
| 6 Плотность $\rho_4^{20}$ | 0.777—0.830 | 0.780—0.850 | 0.810 | 0.826 | 0.785 | 0.786—0.826 |
| 7 Фракционный состав: | | | | | | |
| 8 10% выкипает при температуре в °С не выше 3 | 210 | 210 | 164 | 203 | 165 | 210 |
| 9 50% то же | — | — | 192 | 215—223 | 185 | — |
| 90% » | 255 | — | 225 | 241—254 | 216 | — |
| 10 к. к. в °С не выше | 300 | 288 | 248 | 288 | 241 | 288 |
| 11 Вязкость кинематическая в *сст* при температуре —40° С не более | 10 5 | 16 6 | 8.29 | 10.8—12.1 | 7.25 | 6.0 5 |
| 12 Температура кристаллизации в °С не выше | —60 5 | —40 | Ниже —60 | —47—48 | —40—60 | Ниже —40 |
| 13 Температура вспышки в °С не ниже | 40 | 60 | 48 | 61—64 | 42—54 | 68 |
| 14 Содержание ароматических углеводородов в % не более | 20 | 25 | 14.3 | 20.3—21 | 19.1 | 20 |
| 15 Содержание серы в % не более | 0.2 | 0.4 | 0.079 | 0.33 | 0.037 | 0.2 |
| 15A » меркаптановой серы в % не более | 0.005 | 0.001 | 0.0009 | 0.001 | — | — |
| 15B » антиокислителя в *мг/л* не более | 24 | 24 | — | — | — | — |
| 16 Содержание олефиновых углеводородов в % не более | 5.0 | 5.0 | 1.0 | 1.0 | — | — |
| 17 Теплотворная способность в *ккал/кг* не ниже | 10 160 | 10 160 | 10 300 | 10 250 | 10 280 | 10 270 |
| 18 Содержание фактических смол в *мг*/100 *мл* не более | 5 | 7 6 | 1.94 | 1÷2.0 | 2.0 | — |
| 19 Потенциальные смолы после 16 час. окисления в *мг*/100 *мл* не более | 8 | 14 | 1.5 | 1.0 | — | — |
| 20 Точка дымления в *мм* не менее | — | 20 | — | — | — | — |
| 21 Проба на медную пластинку | 28 Незначительная | | 27 Выдерживает | | | |
| 22 Упругость паров, *мм* рт. ст. | | | | 26 | 6—55 | 55 |
| 23 Кислотное число в *мг* КОН/*г* не более | | 0.1 | 0.05 | 0.05 | 0.1 | — |
| 24 Бромное число в *г* брома/100 не более | | 5.0 | 0.95 | 4.3 | 0.35 | — |
| 25 Содержание воды в *мг/л* не более | | 1 7 | — | отс | — | — |
| 26 Термическая стабильность по методу CFR: | | | | | | |
| а) перепад давления на фильтре при 204° и 260°, *мм* рт. ст. | — | —8 | — | — | — | — |
| b б) количество отложений в подогревателе, баллы | — | — | — | — | — | — |

1) According to technical standards of Switzerland – grade 2, Italy – AM/C-141, Canada – grade 3 – GR-23; 2) the limitations "not above," "not below," etc., refer solely to the technical standards; 3) for English, French, and Swiss fuel – no more than 6 centistokes at -18°; 4) at -34°; 5) for English and French fuel – no more than -40°, for Swiss fuel, -55°; 6) for English fuel, 10 mg is permitted; 7) not regulated for American fuel; 8) for American JP-5 fuel it is determined, but not standardized.

1) Physical-chemical characteristics; 2) technical standards; 3) grade; 4) Great Britain; 5) France; 6) density $\rho_4^{20}$; 7) fractional composition; 8) 10% evaporates at temperature, °C, no more than; 9) 50%, the same; 10) end point, °C, no more than; 11) kinematic viscosity, centistokes, at temperature of -40°C, no more than; [Key continued on next page]

[Key to Table 145 continued]: 12) crystallization point, °C, no more than; 13) flash point, °C, no less than; 14) content of aromatic hydrocarbons, %, no more than; 15) sulfur content, %, no more than; 15A) content of mercaptan sulfur, %, no more than; 15B) content of antioxidant, mg/l, no more than; 16) content of olefin hydrocarbons, %, no more than; 17) heating value, kcal/kg, no less than; 18) existent gum, mg/100 ml, no more than; 19) potential gum, following 16 hr oxidation, mg/100 ml, no more than; 20) smoke point, mm, no less than; 21) copper-plate test; 22) vapor pressure, mm Hg; 23) acid number, mg KOH/g, no more than; 24) bromine number, g bromine/100, no more than; 25) water content, mg/l, no more than; 26) thermal stability, CFR method: a) pressure drop at filter, 204° and 260°, mm Hg; b) quantity of deposits in heater, arbitrary scale; 27) satisfactory; 28) negligible.

interference with normal fuel injection and the formation of hydrocarbon crystals in it. Owing to the increased crystallization point, it is possible to produce JP-5 fuel in sufficient quantities.

At the present time, the United States is beginning production of new fuels for supersonic aircraft and missiles according to MIL-F-25656 (JP-6) and MIL-F-22524 specifications. These fuels are kerosene-type fuels, and have the following boiling ranges: MIL-F-22656, 120-290°, MIL-F-22524, 150-290°. They possess increased thermal stability and low vapor pressure at high temperatures. The increased thermal stability of these fuels is achieved by improved refining and use of additives [38]. The specific gravity of JP-6 fuel is 0.78-0.86, the crystallization point not above -50° [39]. JP-6 fuel is designed for aircraft flying at speeds of up to Mach 1.5-2.0.

Fuels for TRD in Great Britain. As we can see from Tables 144 and 145, three grades of fuel are produced for TRD in Great Britain; two of them, according to specifications DERD-2482 and DERD-2488 are of the kerosene type, and one, according to specification DERD-2486, is a wide-boiling fuel [28, 40]. English kerosene-type fuels have considerably poorer low-temperature properties, since their crystallization point may reach -40°. The possibility of such an increase in the crystallization point is associated with fact that in England, jet aircraft do not operate under cold winter conditions at low temper-

TABLE 146

Standardized Fuels for TRD in NATO Countries

| 1 Физико-химические показатели | НАТО-F-33 | | НАТО-F-42 | | НАТО-F-40 | |
|---|---|---|---|---|---|---|
| | 2 типа керосина | | | | 3 типа широкой фракции | |
| | MIL-F-5616c JP-1 | DERD-2482 JP-1B | MIL-F-5624c JP-5 | DERD-2488 JP-5B | MIL-F-5624c JP-4 | DERD-2486 JP-4B |
| 4 Плотность $\rho_4^{20}$ | 22 Не выше 0,845 | 0,777—0,830 | 0,749—0,843 | 0,780—0,850 | 0,742—0,802 | 0,736—0,821 |
| 5 Фракционный состав, °С: | | | | | | |
| 6 10% не выше | 210 | —22 | 210 | 210 | — | — |
| 7 20% не ниже | — | Не выше 200 | — | — | 144 | 144 |
| 50% » » | —22 | — | — | — | 188 | 188 |
| 90% » » | Не выше 255 | — | — | — | 243 | 243 |
| 8 к. к. в °С не более | 300 | 300 | 288 | 288 | — | — |
| 9 Остаток в % не более | 1,5 | 1,5 | 1,5 | 1,5 | 1,5 | 1,5 |
| 10 Потери в % не более | 1,5 | 1,5 | 1,5 | 1,5 | 1,5 | 1,5 |
| 11 Вязкость кинематическая, в *сст* при температуре —40° не более | 10 | 6 * | 16,5 ** | 16,5 ** | — | — |
| 12 Кислотность в *мг* КОН/*г* не более | — | 0,1 | — | — | — | 0,1 |
| 13 Температура кристаллизации в °С не выше | —60 | —40 | —40 | —40 | —60 | —60 |
| 14 Температура вспышки в °С не ниже | 43 | 38 | 60 | 60 | — | — |
| 15 Бромное число в *г* брома на 100 *г* не более | 3 | — | — | 3 | — | 5 |
| 16 Содержание ароматических углеводородов в % не более | 20 | 20 | 25 | 25 | 25 | 25 |
| 17 Содержание непредельных углеводородов в % не более | — | — | 5 | — | 5 | 5 |
| 18 Содержание серы, % | 0,2 | 0,2 | 0,4 | 0,4 | 0,4 | 0,4 |
| 19 В том числе меркаптановой серы в % не более | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 |
| 20 Содержание воды в *мг/л* не более | — | 2 | - | 1 | — | 1 |
| 21 Содержание антиокислителя в *мг/л* не более | — | — | 24 | 24 | 24 | 24 |
| 23 Содержание дезактиватора металла в *мг/л* не более | — | — | — | — | 5,6 | 5,6 |
| 24 Содержание фактических смол в *мг*/100 *мл* не более | 5 | 5 | 7 | 10 | 7 | 7 |
| 25 Теплотворная способность низшая в *кал/кг* не менее | — | 10 160 | 10 160 | 10 160 | 10 220 | 10 220 |
| 26 Упругость паров, *кг/см²* | 29 Незначительная | | | | 0,14—0,21 | 0,14—0,21 |

TABLE 146 (continued)

| | | | | | | |
|---|---|---|---|---|---|---|
| 27 Проба на медную пластинку | | | 30 Выдерживает | | | |
| 28 Точка дымления в мм не ниже | – | – | 20 | – | – | – |

*At -18°.
**At -34°.

1) Physical-chemical characteristics; 2) kerosene type; 3) wide-boiling type; 4) density $\rho_4^{20}$; 5) fractional composition, °C; 6) 10%, not above; 7) 20%, not below; 8) end point, °C, not above; 9) residue, %, not above; 10) losses, %, not above; 11) kinematic viscosity, centistokes, at temperature of -40°, not above; 12) acidity, mg KOH/g, not above; 13) crystallization point, °C, not above; 14) flash point, °C, not below; 15) bromine number, g bromine per 100 g, not above; 16) content of aromatic hydrocarbons, %, not above; 17) content of unsaturated hydrocarbons, %, not above; 18) sulfur content, %; 19) including mercaptan sulfur, %, not above; 20) water content, ml/l, not above; 21) content of antioxidant, mg/l, not above; 22) not above; 23) content of metal deactivator, mg/l, no more than; 24) existent gum, mg/100 ml, not above; 25) low heating value, kcal/kg, not less than; 26) vapor pressure, kg/cm$^2$; 27) copper-disk test; 28) smoke point, mm, not less than; 29) negligible; 30) satisfactory.

tures.

In Great Britain, great attention is paid to the water content of the fuel, since the water, liberated from the fuel under operating conditions, corrodes fuel-system parts. Thus, English specifications for TRD fuel provide for the possible presence of dissolved water in the fuel in an amount not exceeding 1-2 mg/l.

English wide-boiling type fuel is the same in its characteristics as the American JP-4 fuel.

Fuel for TRD in France and other countries. The basic fuels used for TRD in France are the wide-boiling fuel of specification Air 3407, and the kerosene-type fuel Air 3405 (Tables 144 and 145) [41]. In their characteristics, French TRD fuels are the same as the English DERD-2482 and DERD-2486. In addition to domestic fuels, the French

use the American JP-1 and JP-4 fuels, as well as the English fuels mentioned.

Belgium, Italy, Switzerland, and Austria use mainly the English DERD-2486 and DERD-2482 fuels for TRD. This is due to the fact that the national companies of these countries produce chiefly English TRD where numbers of engines are needed.

In Italy, the following national specifications apply to TRD fuels: AM/C-142, for wide-boiling fuel and AM/C-141 for kerosene-type fuel. The fuels have the same qualities as the English and American fuels. Italy also makes wide use of American TRD fuels [42].

In Canada, both English and American kerosene-type and wide-boiling fuels are used for TRD. There also exist Canadian national specifications for TRD fuels: 3-GR-23 for kerosene-type fuel, and 3-GR-22A for wide-boiling fuel.

In Switzerland, in addition to English fuels, kerosene-type fuels (grade 2) and wide-boiling fuels (grade 1) are used in accordance with the Swiss state specification (Tables 144 and 145) [43]. Swiss kerosene-type fuel is considerably better than English or French with respect to the low-temperature properties. Thus, the crystallization point of this fuel reaches $-55^{\circ}$. As far as the other characteristics are concerned, no substantial differences among the fuels are observed.

Fuels for TRD in NATO countries. In order to achieve standardization in the countries belonging to NATO, standardized fuels have been adopted for TRD; their characteristics are given in Table 146 [44]. Two kerosene-type fuels (specifications NATO-F-33 and NATO-F-42) and one wide-boiling fuel (specification NATO-F-40) have been adopted as standard fuels in the NATO countries. The specifications for standard TRD fuels for the NATO countries are based upon specifications for the

American JP-1, JP-4, and JP-5 fuels, as well as specifications for the English DERD-2482, 2486, and 2488 fuels.

Fuels for Turboprop Engines

As a rule, the same fuels are used for both TVD and TRD. This is due to the fact that the mixture-formation and combustion processes take place in the same way in TVD and TRD. Owing to the fact, however, that TVD are installed on aircraft designed to fly at lower heights and speeds than aircraft with TRD, it is considered possible to use, in the main, lighter fuels for these engines, for example, gasoline or wide-boiling types. Thus, in the United States and in many other countries, JP-4 wide-boiling fuel is widely used for TVD.

Fuels for Ramjet Engines

In connection with the fact that PVRD are intended chiefly for jet aircraft and missiles flying at considerable supersonic speeds at high altitudes, it is of great importance to provide stability of fuel combustion under these conditions. Accordingly, it had previously been assumed that fuels for PVRD should consist of gasoline or other light petroleum fractions. Thus, nonethylated aviation gasoline was used in the United States and England for PVRD.

The present-day views on fuels for PVRD are different. This was furthered by successful work on ensuring stable combustion in PVRD of not only light fuels, but of heavy fuels as well. As a result of this work, it became possible to use kerosene and gas-oil fuel types in PVRD. The desirability of using heavy fuels for PVRD is also conditioned by the fact that there is limited storage space for fuels on board supersonic flying craft using PVRD and the fact that under supersonic-flight conditions, the fuel is vigorously heated.

Accordingly, the United States presently uses grade RJ-1 heavy kerosene for PVRD; this material possesses increased thermal stabi-

good combustion characteristics, and considerable density (0.84-0.86). This fuel evaporates in the 200-320° range, has a crystallization point not above −40°, and a flash point not below 88° [40].

STARTING FUELS FOR VRD

Starting of a VRD depends to a high degree upon the temperature of the surrounding medium and fuel quality. At low temperatures, it is difficult to start an engine using a heavy fuel of the kerosene or gas-oil type, owing to the inadequate volatility of these fuels. Thus, many VRD are started with special low-boiling starting fuels of the kerosene type, possessing the required volatility at low temperatures. These fuels most frequently take the form of nonethylated aviation gasolines, or mixtures of such gasolines with the basic fuel.

TABLE 147

Starting Fuels for VRD in the United States and England

| 1 Физико-химические показатели | 2 DERD-2485 (Англия) | MIL-F-3572 (США) |
|---|---|---|
| 3 Фракционный состав, °С: | | |
| 4 10% не выше | 75 | 75 |
| 50% » » | 105 | 108 |
| 90% » » | 135 | 135 |
| 5 к. к. в °С не выше | 180 | 180 |
| 6 Упругость насыщенных паров, мм рт. ст. | 300–380 | 300–380 |
| 7 Содержание этиловой жидкости | 9 Отсутствует | 11 |
| 8 Цвет | 10 Бесцветный | Прозрачный |

1) Physical-chemical characteristics; 2) England; 3) fractional composition, °C; 4) 10%, not more than; 5) end point, °C, no more than; 6) saturated vapor pressure, mm Hg; 7) content of ethyl mixture; 8) color; 9) none; 10) colorless; 11) clear.

In the United States and England, aviation gasolines with any octane number are used to start VRD; 1% aviation oil is added. The characteristics of these fuels are shown in Table 147. The use of ethylated aviation gasolines as starting fuels is prohibited.

At the present time, it is also proposed to use as starting fuels

self-igniting fuels such as trimethyl aluminum, or a mixture of this substance with triethyl aluminum. Trimethyl aluminum has a heating value of 10,000 kcal/kg, a crystallization point of $-39^{\circ}$. In flight tests, it ignited the working fuel after flameout to altitudes of 16 km. It is suggested that trimethyl aluminum will start VRD to altitudes of 40 km. At the present time, self-igniting fuels are in the test stage, and are produced only in small quantities [45, 46, 47, 48].

FUEL STANDARDS FOR VRD

The variety of commercial fuels presently produced for VRD, which differ considerably among themselves both as to fraction and chemical composition have made it necessary to select from among them certain grades that may serve as standards in carrying out acceptance and pulsed-repair tests of VRD, and also in carrying out scientific-research work.

In England, grade RT-2978 kerosene fuel is used as such a standard; this material is obtained by direct distillation. A characteristic feature of the English standard fuel (Table 148) is the rigorous determination of the fractional, chemical, and element composition, as well as the other physical and chemical characteristics (sulfur, gum, heating value, etc.) [28].

In the United States, the wide-boiling JP-4 fuel has been adopted as a standard in accordance with the Mil-F-5624B specification; this is a mixture of straight distillates with cracking distillates. The choice of grade JP-4 fuel as a standard is connected with the fact that in the United States this fuel has found wide utilization. Moreover, JP-4 fuel is closest in composition to the so-called "war-time fuel," and is thus considered desirable to conduct all VRD tests with this fuel.

TABLE 148

Fuel Standards for VRD

| 1Физико-химические показатели | 2 RT-2978 (Англия) | MIL-F-5624B (США) |
|---|---|---|
| 3 Плотность $\rho_4^{20}$ | 0,790 | 0,754—0,811 |
| 4 Фракционный состав: | | |
| 5 Температура начала перегонки, °С | 155 | 63 |
| 6 10% выкипает при температуре, °С | 177 | 93 |
| 7 90% то же | 249 | 232 |
| 8 к. к., °С | 271 | 270 |
| 9 Групповой химический состав, %: | | |
| 10 ароматические углеводороды | 19,4 | 18,0 |
| 11 нафтеновые » | 39,2 | } 76,0* |
| 12 парафиновые » | 41,4 | |
| 13 Содержание серы, % | 0,037 | 0,38 |
| 14 Бромное число, *г* брома на 100 *г* | 1,0 | 5,0 |
| 15 Фактические смолы, *мг*/100 *мл* | 5,0 | 3,0 |
| 16 Температура кристаллизации, °С | —42 | — |
| 17 Теплотворная способность, *ккал/кг* | 10 276 | 10 220 |
| 18 Кинематическая вязкость, *сст*: | | |
| 19 при температуре 37,8° С | 1,54 | — |
| » » 17,7° С | 4,29 | — |
| 20 Элементарный состав, %: | | |
| C | 85,8 | — |
| H | 14,2 | — |

*6% unsaturated hydrocarbons.

1) Physical-chemical characteristics; 2) England; 3) density $\rho_4^{20}$; 4) fractional comsition; 5) initial distillation point, °C; 6) 10% evaporated at temperature, °C; 7) 90%, the same; 8) end point, °C; 9) group chemical composition, %; 10) aromatic hydrocarbons; 11) naphthenes; 12) paraffins; 13) sulfur content, %; 14) bromine number, g bromine per 100 g; 15) existent gum, mg/100 ml; 16) crystallization point, °C; 17) heating value, kcal/kg; 18) kinematic viscosity, centistokes; 19) at temperature of 37.8°C; 20) element composition, %.

T-1 fuel is used as the standard fuel, normally, in the USSR.

FUELS FOR VRD IN CIVIL AVIATION

As a rule, in civil aviation the fuels used for VRD have first gained acceptance in military aviation. In recent years, however, the question of fuels for civilian aircraft with VRD has been discussed widely [49, 50, 51, 52]. The reason for this appears to be the fact that not all of the requirements imposed upon a fuel from the viewpoint of military aviation apply with equal force to civil aviation

TABLE 149

Specifications for VRD Fuel for Civil and Military Aviation

| 1 Показатели | 2 Требования к топливу | |
|---|---|---|
| | 3 военной авиации | 4 гражданской авиации |
| 5 Температура кристаллизации, °С | 12 —60 | 16 —40 |
| 6 Воспламеняемость (пожароопасность) | Второстепенное значение | Минимальная |
| 7 Ресурсы | Максимальные | Средние |
| 8 Стоимость | 14 Средняя | 14 Минимальная 16 |
| 9 Испаряемость (ее влияние на сгорание) | Максимальная полнота сгорания | |
| 10 Стабильность при хранении | 15 без образования отложений | |
| 11 Теплотворная способность | 1—2 года | |
| | 13 Максимальная | |

1) Characteristics; 2) fuel requirements; 3) military aviation; 4) civil aviation; 5) crystallization point, °C; 6) inflammability (fire hazard); 7) resources; 8) cost; 9) volatility (its effect upon combustion); 10) stability in storage; 11) heating value; 12) of secondary importance; 13) maximum; 14) moderate; 15) maximum completeness of combustion without formation of deposits for 1-2 years; 16) minimum.

(Table 149). Fuels for VRD in civil aviation should have decreased fire hazard, minimum cost, and average low-temperature properties (crystallization temperature not above $-40^{\circ}$).

The question of which fuel is best suited to civil aviation has been studied for a long period of time: wide-boiling fuel or kerosene-type fuel.

These studies have resulted in divided opinions. Thus, in England it is considered the best fuel for civilian aircraft using VRD is kerosene-type fuel, while in the United States, on the other hand, wide-boiling fuel is thought best. In Soviet civil aviation, the T-1 and TS-1 kerosene-type fuels are widely used at present.

CHEMICAL COMPOSITION OF VRD FUELS

Fuels for VRD consist of petroleum fractions boiling in the 65-350° range, i.e., gasoline, naphtha, kerosene, and for supersonic aircraft, gas-oil fractions.

Chemical composition has a considerable effect upon the operati

characteristics of VRD fuels. Certain classes of hydrocarbons such as the aromatic, the normal paraffin, and the unsaturated have a negative effect upon engine characteristics and fuel quality. An increased content of aromatic hydrocarbons increases the carbon-forming ability of the fuel, normal paraffin hydrocarbons raise the crystallization point, and unsaturated hydrocarbons decrease fuel stability under storage conditions. As a result, in existing technical specifications for VRD fuels, the amount of aromatic hydrocarbons contained in the fuel is limited to 20-25%, the unsaturated hydrocarbons to 2-3.0%, while the presence of normal paraffin hydrocarbons is limited by the low freezing point of $-60^{\circ}$.

Accordingly, the modern VRD fuels T-1, TS-1, T-2, and T-5 contain only from 15 to 20% aromatic hydrocarbons, and the amount established by the standard is not exceeded. Isoparaffin hydrocarbons are present in the fuels in amounts of 33-61%, naphthene hydrocarbons in amounts of 21-45%. The relationship of the aromatic, paraffin, and naphthene hydrocarbons in the fuel, depends, within the limits shown above, upon the nature of the refined petroleum. The content of unsaturated hydrocarbons in fuels for VRD varies from 1.0 to 3.0%.

Among the aromatic hydrocarbons in VRD fuels, the least desirable are the bicyclic hydrocarbons, which have a very great ability to form carbon [4]. Droegumueller and Nilson [53] have shown that in order to prevent excessive carbon formation and to decrease engine smoking in takeoff, the bicyclic aromatic hydrocarbons should not be present in the fuel in amounts greater than 3%.

The amount of gummy material contained in VRD fuels is also limited, as they can considerably decrease the thermal stability of the fuels. According to existing standards, the so-called existent gum, which to a certain degree characterizes the amount of gummy substances

contained in a fuel, should not exceed 8-11 mg/100 ml.

Sulfur compounds are undesirable constituents of VRD fuels; this applies especially to the mercaptans, which cause vigorous corrosion of engine fuel-system parts. Thus, the total amount of sulfur in VRD fuels is limited to 0.2-0.4%, while the mercaptan-sulfur content is held to 0.001-0.01%.

Despite these limitations, fuels for VRD may differ considerably in their chemical compositions. This will depend upon differences in the fuel fractional composition, method by which they are produced, and the origin of the crude used in their preparation [54-61].

Hydrocarbons of various types and structures form the basis for modern VRD fuels. Oxygen, gummy, and sulfur compounds are normally present in fuels in amounts not exceeding 1.0%; even in such small quantities, however, they have a substantial effect upon fuel performance.

Gummy and Oxygen Compounds

Gummy and oxygen compounds are contained in straight-distilled VRD fuels in quantities not exceeding 0.15%. In fuels containing thermal-cracking components, the amount of these compounds present may reach 1.0%. It is clear from Table 150 that the amount of oxygen and gummy compounds in straight-distilled fuels is less by a factor of 8-10 than in fuels containing thermal-cracking components. Despite this fact, oxygen and gummy compounds greatly impair the thermal stability of T-2, TS-1, and T-1 fuels. Separation of the oxygen and gummy compounds from the fuels aids in sharply decreasing the deposit-forming ability of the fuels for VRD at elevated temperatures [9]. The chemical composition of oxygen and gummy compounds in VRD fuels has been studied by Ya.B. Chertkov and V.N. Zrelov [9, 10]. Oxygen and gummy compounds were separated from the VRD fuels by chromatography with

TABLE 150

Content of Oxygen and Gummy Compounds in Fuels for VRD

| 1 Топлива | 2 Содержание кислородных и смолистых соединений в топливе, мг/100 мл | 3 Состав, % (отн.) | |
|---|---|---|---|
| | | 4 кислородных соединений | 5 смолистых * соединений |
| 6 Т-2 грозненское | 92 | 86 | 14 |
| 7 ТС-1 туймазинское | 80 | 84 | 16 |
| 8 Т-1 бакинское | 121 | 79 | 21 |
| 9 Бакинский керосин термического крекинга | 1267 | 62 | 38 |
| 10 Туймазинский керосин термического крекинга | 497 | 69 | 31 |

*We include among the gummy compounds oxidation products that are not driven off in vacuum at 1-2 mm Hg.

1) Fuels; 2) content of oxygen and gummy compounds in fuel, mg/100 ml; 3) composition, % (relative); 4) oxygen compounds; 5) gummy compounds; 6) T-2, Grozniy; 7) TS-1, Tuymazy; 8) T-1, Baku; 9) Baku kerosene, thermal cracking; 10) Tuymazy kerosene, thermal cracking.

silica gel. They take the form of viscous, dark-brown liquids with high molecular weight, roughly twice the molecular weight of the fuel from which they are taken. Oxygen and gummy compounds are characterized by high iodine and hydroxyl numbers. They contain a considerable quantity of esteric and acid substances.

The basic component of oxygen compounds in VRD fuels are alcohols, of which no more than 25% combine with a carboryl group. The alcohols contained in the fuels have a single aromatic ring in their structure; in its side chain, there is a single double bond, and a single hydroxyl group. They have almost no negative effect upon the operating qualities of VRD fuels.

The gummy compounds have the worst effect upon the operating qualities of VRD fuels. In VRD fuels, there are neutral and acid gummy

compounds.

Neutral gums are predominant among the gummy compounds in VRD fuel; they form 95-97% of the entire amount of gum. The neutral gums are characterized by high hydroxyl numbers (275) and iodine numbers (90), which indicates that there is a single double bond in the molecule of neutral gums, and that there is a single hydroxyl group. The neutral gums are chiefly products of alcohol polymerization.

An investigation of the effect of neutral gums on the acidity of VRD fuels has shown that they have no noticeable effect. As far as the acid gums are concerned, they greatly intensify fuel oxidation, even when present in small quantities. A similar effect upon fuel acidity is shown by the hydroxy acids. In VRD fuels, the hydroxy acids are dark-brown liquids of the gummy type; they are contained in the fuel in small amounts.

Sulfur Compounds

Sulfur compounds in VRD fuels are normally present in small quantities. The maximum total sulfur content in VRD fuels does not exceed 0.25-0.4%. Sulfur compounds in VRD fuels form two groups: active (elementary sulfur, hydrogen sulfide, and the mercaptans) and inactive (sulfides, disulfides, thiophanes, thiophenes, and the so-called residual sulfur).

In view of the fact that the active sulfur compounds corrode fuel-apparatus elements in VRD, their content in a fuel is strictly limited. Thus, there should be no more than 0.01-0.005% mercaptan sulfur in a fuel. Hydrogen sulfide and elementary sulfur should be almost completely absent, and this is checked by tests on lead paper and a copper plate.

The chemical composition of sulfur compounds in VRD fuels is shown in Table 151.

It follows from the data given that the major portion of the sulfur compounds in VRD fuels is allotted to the residual sulfur, which so far has not been characterized in depth. An investigation of the effect of residual sulfur on corrosive aggressiveness and thermal stability of VRD fuels has shown that it has practically no influence upon these fuel properties.

Owing to the fact that there is normally no hydrogen sulfide or elementary sulfur in VRD fuels, the corrosion aggressiveness of the fuels is determined chiefly by the mercaptans present in the fuels. Aliphatic and aromatic mercaptans may be present in VRD fuels. The aliphatic mercaptans, contained chiefly in the straight-distilled TS-1 and T-2 fuels [7, 62] display the greatest corrosion aggressiveness. In fuels with thermal-cracking components, it is basically the aromatic mercaptans that are contained; they are not corrosive with respect to copper alloys. This situation has found confirmation in the work of I.Ye. Bespolov and Ye.E. Kolotushkin as well [19].

The sulfides present in VRD fuels are aliphatic and aromatic in nature. The distribution of aromatic and aliphatic sulfides, as Table

TABLE 151

Chemical Composition of Sulfur Compounds in VRD Fuels

| 1 Топливо | 2 Содержание соединений серы, % | | | | | | |
|---|---|---|---|---|---|---|---|
| | 3 общая | серово-4дород | элемен-5тарная | 6 меркаптаны | 7 дисульфиды | 8 сульфиды | 9 остаточная |
| ТС-1 . . . | 0,240 | 10 Нет | 10 Нет | 0,004 | 0,051 | 0,032 | 0,153 |
| Т-2 . . . . | 0,220 | » | » | 0,005 | 0,009 | 0,015 | 0,191 |

1) Fuel; 2) sulfur-compound content, %; 3) total; 4) hydrogen sulfide; 5) elementary; 6) mercaptans; 7) disulfides; 8) sulfides; 9) residual; 10) none.

152 shows, is in many ways similar to the distribution of the mercaptans. In other words, aliphatic sulfides predominate in straight-dis-

TABLE 152

Composition of Sulfides in VRD Fuels

| 1 Топлива прямой гонки | 2 Сульфиды, % | |
|---|---|---|
| | 3 ароматические | 4 алифатические |
| 6 ТС-1 | 5 Отсутствуют | 47,50 |
| 6 ТС-1 | 7,08 | 26,50 |
| Т-2 | 8,97 | 63,00 |

1) Straight-distillation fuels; 2) sulfides, %; 3) aromatic; 4) aliphatic; 5) none; 6) TS-1.

tilled fuels, and aromatic sulfides in fuels containing thermal-cracking components. An increase in sulfide content for VRD fuels leads to a drop in their thermal stability. The aromatic sulfides have the greatest influence upon the decrease in thermal stability of VRD fuels. As the VRD fuel boiling point goes up, the amount of aromatic sulfides increases, and the aliphatic sulfide content drops. Among the sulfides in VRD fuels, a significant proportion is represented by derivatives of thiophane and thiophene, in the mono-, bi-, and tricyclic forms [63, 64].

The amount of disulfides present in VRD fuels depends upon the origin of the crude petroleum. Thus, no disulfides were found in TS-1 fuel refined out of petroleum from carboniferous deposits of the Tuymazy area [63]. Some of the disulfides are members of compounds that increase the thermal stability of the fuels.

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[List of Transliterated Symbols]

651 пол = pol = polet = flight

651 ВРД = VRD = vozdushno-reaktivnyy dvigatel' = air reaction engine

653 ПВРД = PVRD = pryamotochnyy vozdushno-reaktivnyy dvigatel' = ramjet engine

653 СПВРД = SPVRD = sverkhzvukhovoy PVRD = supersonic ramjet engine

654 ТРД = TRD = turbokompressornyy vozdushno-reaktivnyy dvigatel' = turbojet engine

654 ТВД = TVD = turbovintovoy dvigatel' = turboprop engine

655 ДТРД = DTRD = dvukhkonturnyy vozdushno-reaktivnyy dvigatel' = double-flow or ducted-fan engine

## Chapter 21

## OPERATING CHARACTERISTICS OF FUELS FOR AIR-REACTION ENGINES

The development of modern aviation using air-reaction engines (VRD), conversion of aircraft to supersonic flight speeds at high altitudes have shifted the following operating properties to the leading position: energy characteristics (heating value, density, completeness of combustion), thermal stability, carbon-formation ability, and viscosity-temperature characteristics. In addition to these properties, as before, much attention is devoted to volatility, corrosion aggressiveness, stability in storage, fire resistance, solubility of air and water in fuels, as well as the starting and low-temperature characteristics of fuels for VRD.

The operating characteristics of fuels for VRD can be classified into two basic groups: first group – characteristics affecting the operation of the VRD fuel system, and the second group – characteristics affecting the operation of the combustion chamber, gas turbine, and other elements of the engine gas-air system.

In the present chapter, we shall consider the effect of certain fuel properties on both fuel-system operation and the operation of elements in the engine gas-air system.

### EFFECT OF FUEL QUALITY UPON OPERATION OF VRD FUEL SYSTEM

In modern VRD, the fuel is supplied to the combustion chamber in quantities of from 200 to 8000 liter/hr at a pressure of 1.4-55.0 $\frac{kg}{cm^2}$, as determined by the design and operating regime of the engine. The

thrust of a VRD varies as a function of the variation of the amount of fuel supplied. With the throttle control kept in the same position, the fuel flow rate should be maintained constant under any conditions, either in flight at high altitudes at subsonic speeds under low-temperature conditions, or in flight at supersonic speeds under conditions of considerable aerodynamic heating. The following factors affect the variation in fuel flow rate in this case:

1) formation of vapor locks;

2) liberation of air dissolved in the fuel;

3) fuel crystallization;

4) crystallization of water dissolved in fuel;

5) corrosive effect of fuel upon fuel-system elements;

6) formation of sediments not dissolved in fuel.

Accordingly, we shall consider the effect of fuel quality upon the phenomena mentioned above.

Effect of Fuel Quality Upon Losses Due to Evaporation and Formation of Vapor Locks

Fuel volatility greatly affects uninterrupted operation of a VRD. Modern aircraft with VRD have high climb rates. As a result, the fuel temperature in the tanks is almost unchanged during the climb, and remains approximately equal to the temperature at takeoff. Thus, in a climb to a height of 12.2 km, the fuel temperature in subsonic aircraft drops by only from 19° to 16° (Fig. 194) [1].

In flight tests of the American wide-boiling JP-3 fuel in climbing, its evaporation at the initial temperature of 43° was so vigorous that after a certain period of time, the fuel was observed to boil; this was accompanied by loss of fuel from openings in the fuel tank. As a result, fuel losses amounted to from two-thirds to three-quarters of all the fuel in the fuel tanks [2]. This phenomenon was not obse-

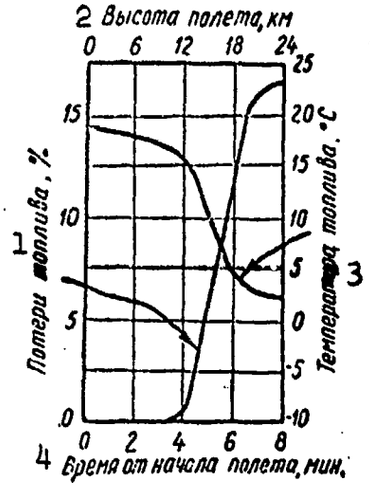



Fig. 194. Variation in temperature and losses owing to evaporation of gasoline-type fuel as a function of altitude. 1) Fuel losses, %; 2) altitude, km; 3) fuel temperature, °C; 4) time from initiation of flight, min.

in tests of kerosene-type JP-1 fuel in a climb to an altitude of 18.3 km. The basic effect upon fuel loss in subsonic aircraft is due to the flight altitude, initial temperature, and fuel vapor pressure. The climb rate (as we can see from Table 153) has almost no effect upon fuel losses.

The initial fuel temperature has a great effect upon fuel losses in climbing. The higher the initial fuel temperature, the more rapidly at a lower altitude the fuel will boil, and the greater the losses that will be observed at high altitudes.

Up to the present time, a great deal of attention has been devoted in the United States to studying the effect of initial temperature and ambient pressure corresponding to an altitude of up to 15 km of fuel volatility [3].

TABLE 153

Effect of Climb Rate Upon Fuel Losses Owing to Evaporation

| 1 Скорость подъема, м/мин | 2 Потери топлива во время подъема до высоты 18,3 км, % | |
|---|---|---|
| | 3 топливо типа бензина с начальной температурой 20° | 4 топливо типа широкой фракции с начальной температурой 15,5° |
| 1525 | 12.8 | 10.3 |
| 3050 | 15.2 | 10.6 |
| 4590 | 15.0 | 11.5 |
| 6120 | 13.0 | 10.7 |
| 7640 | 15.2 | 10.3 |
| 5 В среднем | 14.2 | 10.7 |

1) Climb rate, m/min; 2) fuel losses during climb to height of 18.3 km, %; 3) gasoline-type fuel with initial temperature [Key continued on next page]

[Key to Table 153 continued]: of 20°; 4) wide-boiling-type fuel, initial temperature 15.5°; 5) average.

TABLE 154

Losses Owing to Evaporation for Various VRD Fuels at Height of 18.3 km

| 1 Топливо | Упругость паров при 37,8°, 2 кг/см² | 3 Потери на высоте 18,3 км (в %) при | |
|---|---|---|---|
| | | 15,5° | 37,8° |
| 4 Типа керосина . . . . . | 7 Ниже 0,007 | 0,0 | 0,0 |
| 5 Типа широкой фракции | 0,136 | 0,0 | 1,0 |
| 6 То же . . . . . | 0,47 | 9,6 | 15,0 |

1) Fuel; 2) vapor pressure at 37.8°, kg/cm²; 3) losses at altitude of 18.3 km (T) at; 4) kerosene type; 5) wide-boiling type; 6) the same; 7) below.

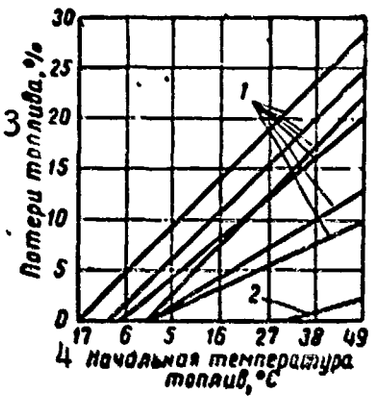



Fig. 195. Effect of initial temperature on losses owing to evaporation for various VRD fuels at height of 18.3 km. 1) Gasoline-type fuel; 2) wide-boiling-type fuel; 3) fuel losses, %; 4) initial fuel temperature, °C.

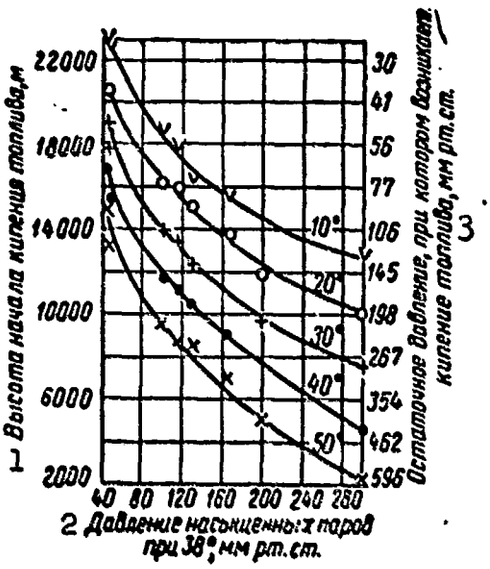



Fig. 196. Relationship among vapor pressure, initial temperature, and height at which VRD fuel begins to boil. 1) Height at which fuel begins to boil, m; 2) saturated vapor pressure at 38°, mm Hg; 3) excess pressure at which fuel boils, mm Hg.

A study of losses for various fuels owing to boiling at a height of 18.3 km (Fig. 195) shows that fuel losses differ for the same in-

tial temperature [1]. This is explained by the difference in the vapor pressures of these fuels. The vapor pressure of a fuel is one of the basic characteristics that determines the flight altitude at which a fuel commences to boil. The relationship between the saturated vapor pressure of a fuel, the initial temperature, and the height at which the fuel boils is shown in Fig. 196 [4]. It is clear from the data given that at an initial temperature of 20°, kerosene-type fuels (T-1, TS-1, etc.) will boil at a height of 20.5 km, while wide-boiling-type fuel with a vapor pressure of 100 mm Hg (T-2) will boil at a height of 16.5 km.

Large losses due to evaporation are observed when the fuel has a high vapor pressure. Fuel losses for vapor pressures greater than 0.136-0.210 kg/cm$^2$ may be considerable even at 37.8°. In fuels having vapor pressures fluctuating from 0.351 to 0.492 kg/cm$^2$, the losses at a height of 18.3 km (Table 154) may reach 10%, even for the case in which the temperature at ground level is 15.5°. If the initial temperature amounts to 37.8°, the losses at a height of 18.3 km may reach 20% [1].

Such great losses at high altitudes cause a change in the composition of the fuel in the tank, since it is chiefly the light fractions that evaporate. This essentially eliminates completely the advantages inherent in a wide-boiling fuel having a vapor pressure of about 0.47 kg/cm$^2$ as a result of the introduction of low-boiling components. Here the vapor pressure, volatility, and detonation points will change. The expansion in VRD fuel resources attained by introducing low-boiling components proves to be illusory.

Since the vapor-formation rate increases considerably in climbing, high pressures appear in the fuel tanks, necessitating a complicated system of valves and openings for reducing the pressure.

TABLE 155

VRD Fuel Vapor Pressure as a Function of Temperature

| 1 Топливо | 2 Упругость паров (в мм рт. ст.) при | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20° | 40° | 60° | 80° | 100° | 120° | 140° | 160° |
| Т-2 . . . . . | 60 | 100 | 150 | 280 | 475 | 760 | — | — |
| Т-1 . . . . . | 30 | 35 | 40 | 80 | 160 | 240 | 440 | 640 |
| Т-5 . . . . . | — | 10 | 20 | 30 | 60 | 90 | 160 | 220 |

1) Fuel; 2) vapor pressure (in mm Hg) at.

TABLE 156

Ratio of Vapor Phase to Liquid Phase as a Function of flight altitude for VRD Fuels at 37.8°

| 1 Топливо | Отношение паровой фазы к жидкой 2 V/l при высоте полета, км | | | | | |
|---|---|---|---|---|---|---|
| | 3 | 4,6 | 5 | 9 | 12 | 16,7 |
| 3 Типа бензина . . . . . | 0,8 | 2,0 | 4,0 | — | — | — |
| 4 Типа керосина . . . . . | 0,1 | 0,1 | 0,2 | 0,4 | — | 2,0 |

1) Fuel; 2) ratio of vapor phase to liquid phase, V/l at a flight altitude in km of; 3) gasoline type; 4) kerosene type.

Losses of fuel due to evaporation may be decreased by two methods: by sealing the tanks, and by cooling the fuel prior to the flight [5].

In addition to large quantitative losses in the VRD fuel system when wide-boiling fuels with high vapor pressures are used, even at low altitudes, vapor locks may form, causing serious interruptions in the operation of the engine fuel system.

When the aircraft is climbing, the pressure at the fuel-pump inlet is reduced, causing a drop in the line excess pressure as compared with the fuel vapor pressure. At a certain altitude, for which the fuel vapor pressure approaches the pressure in front of the pump, the fuel emits vapors vigorously, leading to the formation of vapor locks in the fuel system, and to a sharp drop in the amount of fuel

supplied to the combustion chamber.

Kerosene-type fuels used for VRD have low vapor pressures. When kerosene-type fuel is used for subsonic aircrafts, vapor locks are not formed. It is possible to fly at altitudes greater than 12-14 km without sealing or applying excess pressure to the fuel tanks for kerosene-type fuels (T-1, TS-1, T-5, JP-1, JP-5) that evaporate in the 140-280° range and have vapor pressures below 100 mm Hg. Wide-boiling jet fuels (T-2, JP-4), evaporating in the 60-280° range, and having vapor pressures of 100-150 mm Hg provide reliable aircraft fuel-system operation, without the use of excess pressure in the fuel tanks, only to altitudes of 10-12 km.

For modern supersonic aircraft, the fuel temperature increases in flight owing to the heating of the entire aircraft structure, and the utilization of the fuel as a cooling agent. At the higher temperatures, the fuel vapor pressure rises. For kerosene-type fuels, this increase is slight up to temperatures of 80°, at which point the vapor pressure of wide-boiling-type fuels rises sharply (Table 155). Thus, Walkery [6] has shown that a wide-boiling-type fuel with vapor pressure of 150 mm Hg begins to boil in aircraft tanks at a height of 8.7 km at a temperature of 50°. In the United States, the effect of fuel volatility upon fuel-system operation in supersonic aircraft has been evaluated under laboratory conditions by a determination of the maximum pressure in a special fuel tank at a temperature of 230° [2]. Under such conditions, a tank containing JP-4 fuel developed a pressure of up to 14 kg/cm$^2$, while a gas-oil type fuel produced only 1.2 kg/cm$^2$. The tendency of the fuel to form vapor locks can be determined on the basis of the volumetric ratio of the vapor and liquid phases v/l. The ratio of the volume of vapor phase to the volume of liquid phase depends upon the aircraft flight altitude; it is shown in Table 156. If

we assume that a permissible v/l ratio for a fuel system equals two, then gasoline-type fuel forms vapor locks at a temperature of 37.8° at a height of 4.6 km.

For kerosene-type fuel, vapor locks do not form at this temperature while the aircraft is flying at an altitude of 16.7 km. For supersonic aircraft, in which the fuel may develop temperatures of 120-150° in the fuel system, the formation of vapor locks may set in at a considerably lower altitude, unless a heavier fuel is used, such as type T-5.

Fuel vapor pressure has a substantial effect upon aircraft range, fuel-tank weight, and on the size and operation of the fuel pump. The throughput of a fuel pump working with kerosene-type fuel is approximately double that obtained with gasoline-type fuel having a vapor pressure 0.49 kg/cm$^2$. The decrease in fuel-pump throughput for kerosene-type fuel in climbing, and the drop in fuel-line pressure will be slight (10-15%), while for gasoline-type fuel, the pump flowthrough will decrease by 30-40% [5].

For fuels having high vapor pressure, pumps 2-4 times larger are needed than for kerosene-type fuels. Moreover, gasoline-type fuels require more powerful auxiliary pumps.

Solubility of Air in VRD Fuels

When a jet aircraft climbs rapidly to a high altitude, at a specific moment sudden foaming of the fuel and ejection of part of it from the tank through openings and valves will be observed. These phenomena are connected with the sudden evolution of dissolved air from the fuel. This occurs basically when the engine operates with high-boiling kerosene-type fuels, with a low content of low-boiling components. When an aircraft climbs, dissolved air will also escape from low-boiling fuels; its liberation, however, occurs uniformly dur-

TABLE 157

Solubility of Air in Fuels as a Function of Their Characteristics

| 1 Плотность при 21°, г/см³ | 2 Вязкость при 21°, сст | Поверхностное натяжение при 21°, 3 дн/см | Растворимость воздуха при 21° и 760 мм рт. ст., 4 % объемн. |
|---|---|---|---|
| 0,882 | 898 | 29,3 | 7,75 |
| 0,880 | 368 | 29,5 | 9,05 |
| 0,870 | 17,5 | 26,8 | 9,70 |
| 0,780 | 1,7 | 23,4 | 17,20 |
| 0,723 | 0,6 | 18,4 | 22,80 |

1) Density at 21°, g/cm$^3$; 2) viscosity at 21°, centistokes; 3) surface tension at 21°, dynes/cm; 4) solubility of air at 21° and 760 mm Hg, % by volume.

TABLE 158

Quantity of Air and Rate of Evolution from VRD Fuels in Climbing

| 1 Высота полета, км | 2 Выделение воздуха (в % объемн.) при коэффициенте растворимости | | 3 Скорость выделения воздуха (в мл/100 мл км) из топлива с коэффициентом растворимости | |
|---|---|---|---|---|
| | 0,025 | 0,015 | 0,025 | 0,015 |
| 1,2 | 2,5 | 1,5 | 2,5 | 1,5 |
| 2,4 | 5,0 | 3,0 | 2,5 | 1,5 |
| 3,9 | 7,5 | 4,5 | 2,5 | 1,5 |
| 5,7 | 10,0 | 6,0 | 2,5 | 1,5 |
| 8,1 | 12,5 | 7,5 | 2,5 | 1,5 |
| 11,1 | 15,0 | 9,0 | 2,5 | 1,5 |
| 17,4 | 17,5 | 10,5 | 2,5 | 1,5 |

1) Flight altitude, km; 2) evolution of air (in % by volume) for solubility factor of; 3) rate of evolution of air (in ml/100 ml km) from fuel with solubility factor of.

the flight, and the volume of air liberated is slight in comparison with the volume of fuel vapors forming.

There is relatively little air dissolved in VRD fuels. Gasoline-type fuels have roughly 20 to 25% air in solution, by volume, and kerosene-type fuels from 13 to 15% by volume [1].

An investigation of air solubility in VRD fuels of different chemical compositions has shown that the solubility of air depends

upon the surface tension, density, and viscosity of the fuels. As the surface tension, density, and viscosity increase (Table 157) the solubility of air in the fuels drops. Aromatic hydrocarbons with low boiling points have high surface tension and correspondingly lower air solubility than do paraffin fractions with the same boiling points.

The amount of moisture dissolved in the fuel also affects the solubility of air. In the presence of moisture, the air-solubility factor rises from 0.0191 to 0.021. Consequently, at low atmospheric pressure somewhat more air is liberated from a wet VRD fuel than from a dry fuel.

It has been established that the cause of the sudden liberation of air from a fuel is the state of supersaturation of the fuel by air during the rapid ascent of the aircraft to a great height. For certain heavy hydrocarbon mixtures, it is possible to obtain air supersaturation up to 100%. The vigorous evolution of air from a supersaturated fuel commences at a great height owing to the rapid mixing of the fuel. When the fuel is mixed, the rate of air liberation is several thousand times greater than in a calm state [7].

Experiments have shown that in a fuel tank 90% full at a climb rate of 7620 m/min with constant rapid mixing, air is liberated from saturated kerosene uniformly at an altitude of 2440-3050 m, while at an altitude of 18,300 m, air evolution ceases owing to the onset of equilibrium. Under similar conditions, without mixing, no evolution of air is observed. When the flight ceiling is reached, however, following rapid brief mixing vigorous evolution of air is observed leading to great turbulence in the kerosene, and to the ejection of a part of the fuel from the tank. If only mild mixing of the fuel occurs, vigorous evolution of air is not observed even at the ceiling altitude.

The fuel will not be supersaturated with air if the fuel is vi-

orously mixed while the aircraft is climbing. Here, as we can see from Table 158, the air is given off at a constant rate that is independent of the flight altitude. The absolute quantity of air escaping varies as a function of flight altitude and the solubility of the air in the fuel.

The solubilities in the fuel of the oxygen, nitrogen, and inert gases making up the air differ. At 15.5°, the solubility factor for oxygen in kerosene-type fuel equals 0.0285, and it is 0.0157 for nitrogen. As a result, oxygen is dissolved in the fuel in greater proportions than it is contained in the air. Thus the gaseous mixture evolving from the fuel is richer in oxygen than ordinary air. The volumetric ratio of nitrogen to oxygen amounts to 2.07:1 in this gas, while for air it is 3.76:1. Figure 197 shows that this phenomenon effects the change in the detonation points of mixtures formed with vapors of kerosene-type VRD fuels. It has been established that the gas escaping from a kerosene-type fuel does not create a major explosion hazard. A gas with increased oxygen content, however, is a more aggressive medium with respect to corrosion of materials in the engine fuel-system units than is ordinary air.

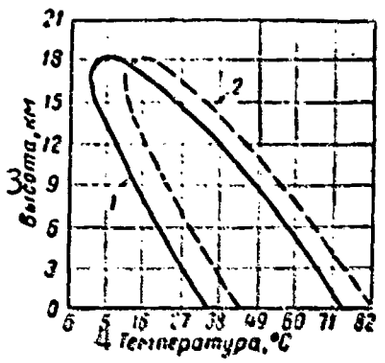



Fig. 197. Detonation limits for mixtures of kerosene-type fuel vapors with ordinary air, and with gas escaping from fuel. 1) With air; 2) with evolving gas enriched with oxygen; 3) height, km; 4) temperature, °C

It has been suggested that foaming of jet fuels be prevented by adding to them fluorine compounds of aliphatic hydrocarbons with from 8 to 30 carbon atoms, boiling at 120-130° (10 mm Hg) [8]. In order to improve the dispersion of sediments of this type, sodium dioctyl sulfosuccinate is added to them. When 0.075% of such additives are pre-

sent in a jet fuel, the column of foam forming at a specific vacuum in the fuel drops from 761 mm to 12 mm.

Corrosion Aggressiveness of VRD Fuels

During operation of VRD, fuels, and especially those with a considerable content of sulfur compounds, cause corrosion of parts in several engine units. Two types of engine corrosion are distinguished:

1) liquid-phase corrosion of fuel-system elements;

2) high-temperature gas corrosion of combustion-chamber walls, exit nozzle, and gas-turbine parts.

Liquid-phase corrosion of fuel-system element parts (fuel pumps, barometric regulator, automatic fuel distributor, filters, throttle valve) is manifested in chemical and electrochemical processes. Chemical corrosion occurs under the direct chemical interaction of corrosive active substances contained in the fuel with metals or alloys used to manufacture fuel-system element parts. Many fuel-system element parts are made from copper, nickel, or their alloys, and many are cadmium plated; all of these materials are liable to chemical corrosion.

Corrosion is most frequently noted in the nonworking surfaces of rotors, the end sections of the servo-piston spring and the fuel-pump input-filter springs, the barostat springs, screen filters, etc.

There have been many studies of the corrosion aggressiveness of VRD fuels in the liquid phase [9, 10, 11].

There has now been developed a complex method for evaluating the corrosion aggressiveness of VRD fuels, which makes it possible to determine not only the weight loss of metal, but also the magnitude of corrosion deposits on a metal surface and the corrosion sediments in fuels [9].

Corrosion under the influence of fuel components

Sulfur compounds are the basic corrosion-active components of VRD fuels. Fuel hydrocarbons and oxygen compounds, however, also affect the corrosion aggressiveness of sulferous fuels. Thus, aromatic hydrocarbons are capable of decreasing considerably the corrosion of certain metals under the influence of organic acids, while paraffin hydrocarbons do not possess this property [12].

Among the sulfur compounds of kerosene distillates, the corrosion-active compounds are hydrogen sulfide, elementary sulfur, and the mercaptans. Commercial VRD fuels contain no hydrogen sulfide after refining. Thus, the corrosion aggressiveness of VRD fuels of the TS-1 and T-2 types depend chiefly upon the elementary sulfur and mercaptans contained in them (Table 159).

Elementary sulfur causes corrosion mainly of fuel-apparatus parts made from copper alloys; cadmium or zinc coatings are not effective. Figure 198 shows graphically the effect of elementary sulfur on corrosion and the amount of corrosion deposits for VB-24 antimony bronze [13]. The data given show that corrosion and deposits on the bronze increase sharply where the elementary-sulfur content of the fuel is greater than 0.002%. The corrosion process is accompanied first by destruction of the bronze surface, and then considerable corrosion deposits, black in color, are formed on the bronze (Table 160); the deposits subsequently separate from the surface and accumulate in the fuel as black insoluble sediments. The more elementary sulfur contained in a fuel, the more vigorously these processes occur.

The process of copper-alloy corrosion under the influence of elementary sulfur cannot be considered just as a process occurring on the metal surface. The study of Ya.B. Chertkov and A.T. Govorov [14] carried out with the aid of radioactive sulfur $S^{35}$ has shown that the

TABLE 159

Corrosion Aggressiveness of VRD Fuels Obtained from Sulfurous Petroleums*

| 1 Топливо | 2 % серы в виде | | Коррозия бронзы 5 ВБ-24, г/м² | 6 Отложения на бронзе, г/м² | 7 Осадки, мг/100 мл |
|---|---|---|---|---|---|
| | 3 элементарной серы | 4 меркаптанов | | | |
| ТС-1 . . . . . | 0,001 | 0,002 | 0,5 | 0,3 | 3,0 |
| 8 То же . . . . | 0,001 | 0,003 | 0,8 | 0,2 | 2,8 |
| » . . . . | 0,002 | 0,006 | 2,5 | 0,6 | 3,4 |
| » . . . . | 0,002 | 0,040 | 7,2 | 1,2 | 8,5 |
| » . . . . | 0,004 | 0,002 | 7,2 | 8,1 | 3,1 |
| Т-2 . . . . . | 0,001 | 0,050 | 8,0 | 0,9 | 3,5 |
| Т-2 . . . . . | 0,004 | 0,003 | 6,5 | 8,0 | 3,7 |

*According to KOC method at 120°.

1) Fuel; 2) % sulfur in form of; 3) elementary sulfur; 4) mercaptans; 5) corrosion of VB-24 bronze, g/m²; 6) deposits on bronze, g/m²; 7) sediments, mg/100 ml; 8) the same.

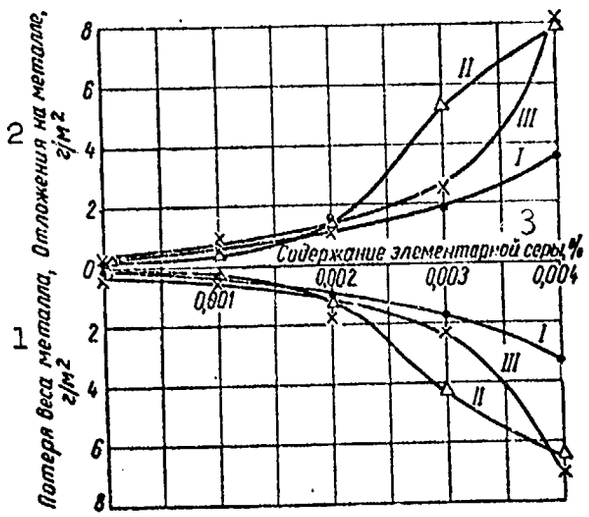
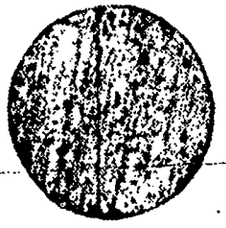
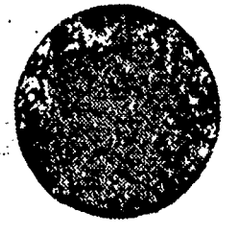
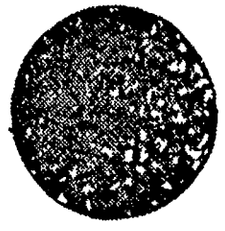
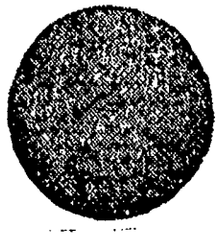



Fig. 198. Effect of elementary sulfur on corrosion and corrosion deposits for VB-24 bronze. I) Baku T-1; II) Grozniy T-1; III) TS-1. 1) Weight loss of metal, g/m²; 2) deposits on metal, g/m²; 3) elementary-sulfur content, %.

basic mass of elementary sulfur in the fuel penetrates within the alloy and then proceeds to interact with its components and to destroy its initial structure. As Table 161 shows, at temperatures of 120 and 150°, about 50-95% of all the elementary sulfur present in the fuel

TABLE 160

Corrosion of VB-24 Bronze Under Influence of Elementary Sulfur

| 1 Концентрация элементарной серы, % | 2 Коррозия, г/м² | 3 Отложения, г/м² | 4 Состояние поверхности |
|---|---|---|---|
| 5 Без элементарной серы | 0 | 0 |  |
| 0,005 | 5,0 | 7,0 |  |
| 0,010 | 8,1 | 12,0 |  |
| 0,015 | 12,0 | 19,0 |  |

1) Elementary-sulfur concentration, %; 2) corrosion, g/m$^2$; 3) deposits, g/m$^2$; 4) surface conditions; 5) no elementary sulfur.

appears within VB-24, VB-24N, and VB-24NTs bronzes. An increase in fuel temperature from 120 to 150° leads to an increase in the migration of sulfur within the alloy. Accordingly, considerably less sulfur accumulates in the deposits forming upon the metal surface at the 150°

TABLE 161

Distribution of Elementary Sulfur in Corrosion of Various Grades of Bronze in VRD Fuel

| 1 Распределение серы после испытания | 2 Бронза ВБ-24 | | | 3 Бронза ВБ-24Н (никелевая) | | | 4 Бронза ВБ-24НЦ (никель-цинковая) | | |
|---|---|---|---|---|---|---|---|---|---|
| | 5 Исходная концентрация элементарной серы в топливе, % | | | | | | | | |
| | 0,002 | 0,004 | 0,006 | 0,002 | 0,004 | 0,006 | 0,002 | 0,004 | 0,006 |
| 6 Температура 120° | | | | | | | | | |
| 8 В сплаве | 84,3 | 84,3 | 75,0 | 83,7 | 62,8 | 50,7 | 86,8 | 90,8 | 92,5 |
| 9 В отложениях | 15,3 | 15,1 | 24,6 | 15,9 | 36,7 | 48,9 | 12,7 | 8,9 | 7,0 |
| 10 В осадках | Следы | 0,1 | 0,1 | 0,3 | 0,2 | 0,1 | 0,1 | 0,1 | 0,1 |
| 11 В топливе | 0,4 | 0,3 | 0,3 | 0,1 | 0,3 | 0,3 | 0,4 | 0,3 | 0,4 |
| 7 Температура 150° | | | | | | | | | |
| 8 В сплаве | 93,1 | 90,3 | 83,7 | 93,5 | 89,5 | 89,8 | 94,6 | 93,7 | 91,8 |
| 9 В отложениях | 6,5 | 9,3 | 15,9 | 6,1 | 10,6 | 9,7 | 5,0 | 5,9 | 7,7 |
| 10 В осадках | 0,1 | 0,1 | 0,1 | 0,1 | 0,1 | 0,1 | 0,1 | 0,1 | 0,1 |
| 11 В топливе | 0,3 | 0,3 | 0,3 | 0,3 | 0,3 | 0,4 | 0,3 | 0,3 | 0,4 |

1) Distribution of sulfur after testing; 2) VB-24 bronze; 3) VB-24N bronze (nickel); 4) VB-24NTs bronze (nickel-zinc); 5) initial concentration of elementary sulfur in fuel, %; 6) temperature 120°; 7) temperature 150°; 8) in alloy; 9) in deposits; 10) in sediments; 11) in fuel; 12) traces.

TABLE 162

Effect of Mercaptan Sulfur on Corrosion Aggressiveness of TS-1 and T-2 Fuel (at 60° after 100 hr)

| 1 Исходное топливо | | 2 Медь | | 3 Бронза ВБ-24 | |
|---|---|---|---|---|---|
| 4 содержание серы, % | | содержание меркаптановой серы после испытания, 7 % | 8 коррозия, г/м² | 9 содержание меркаптановой серы после испытания, % | 10 коррозия, г/м² |
| 5 общей | в том числе 6 меркаптановой | | | | |
| 11 Топливо ТС-1 | | | | | |
| 0,12 | | 12 Отсутствует | | | |
| 0,14 | 0,002 | » | » | » | 1,4 |
| 0,15 | 0,005 | — | — | » | 3,3 |
| 0,17 | 0,010 | — | — | » | 6,8 |
| 0,18 | 0,025 | 0,024 | 0,3 | 0,005 | 9,3 |
| 0,30 | 0,050 | 0,050 | 0,5 | — | 10,8 |
| 13 Топливо Т-2 | | | | | |
| 0,14 | 0,002 | Отсутствует | 0,8 | 11 Отсутствует | 1,1 |
| 0,15 | 0,005 | 11 0,001 | 2,5 | » | 3,5 |
| 0,15 | 0,010 | 0,006 | 3,1 | » | 7,6 |
| 0,17 | 0,025 | 0,015 | 6,2 | 0,004 | 12,3 |
| 0,23 | 0,050 | 0,038 | 9,3 | 0,024 | 14,2 |

[Key on following page]

[Key to Table 162]: 1) Initial fuel; 2) copper; 3) VB-24 bronze; 4) sulfur content, %; 5) total; 6) including mercaptan sulfur; 7) mercaptan-sulfur content after testing, %; 8) corrosion, $g/m^2$; 9) mercaptan-sulfur content after test, %; 10) corrosion, $g/m^2$; 11) TS-1 fuel; 12) none; 13) T-2 fuel.

temperature.

The process of bronze-alloy corrosion under the influence of elementary sulfur occurs so vigorously that nearly all of the elementary sulfur is rapidly taken out of the fuel. VB-24 bronzes act as a sort of "sponge," totally absorbing the elementary sulfur from the fuels. The addition of nickel and zinc alloying elements to VB-24 bronze results in almost no retardation of this process.

Serious operating difficulties appear when fuels are used that have elevated corrosion aggressiveness owing to the presence of mercaptan sulfur in them. Bronze and cadmium parts of VRD fuel apparatus prove to be extremely sensitive to the action of mercaptan sulfur. Thus, under engine operating conditions in areas of high air humidity, the formation of gelatinous deposits on cadmium surfaces of fuel-pump parts has been noticed; in many cases, these deposits disturbed fuel-system operation [15]. During bench tests of TS-1 and T-2 fuels with increased mercaptan-sulfur content, it was noted that corrosion of bronze engine fuel-apparatus parts occurred. As a result, there was abrasion of bronze thrust bearings for pistons, and corrosion deposits formed on the surface of the fuel-pump rotor. A portion of the corrosion deposits, entering the fuel, clogs nozzle passages, impairing dispersion of the fuel and increasing carbon deposits in the combustion chambers. The carbon causes buckling and splitting of fire tubes. Cases were observed in which sediments of corrosion origin disturbed operation of the fuel regulators. Thus, in one case the deposition of corrosion sediments on a governor valve caused a fuel leak, and led to a reduction in engine speed during takeoff.

Mercaptans contained in TS-1 and T-2 fuels chiefly cause corrosion of copper, VB-24 bronze, and cadmium. Steels, aluminum alloys, and Br AZhN-10-4-4 bronze are not subject to corrosion by mercaptans at the ambient air temperature. The corrosion aggressiveness of fuels increases as the mercaptan-sulfur content rises (Table 162) [15].

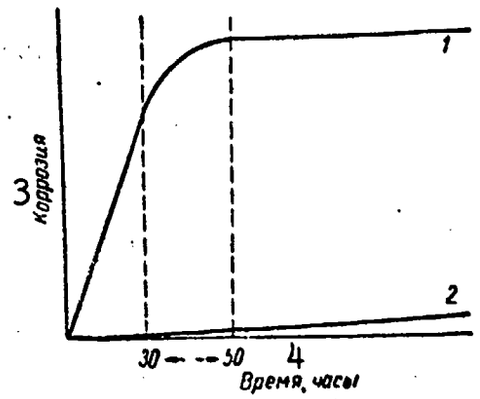



Fig. 199. Corrosion of nonferrous metals and their alloys in VRD fuels at temperatures of 100-120°. 1) Sulfurous TS-1 and T-2 fuels; 2) nonsulfurous T-1 and T-5 fuels; 3) corrosion; 4) time, hr.

VB-24 bronze suffers the most corrosion under the influence of mercaptans. Corrosion of VB-24 bronze is accompanied by a drop in the fuel mercaptan sulfur content. Thus, in fuels containing up to 0.01% mercaptan sulfur, the mercaptans are completely gone after 100 hr. Where the mercaptan sulfur content is greater than 0.025%, only a portion of the mercaptans con-

TABLE 163

Effect of Boiling Range on Corrosion Aggressiveness of Mercaptans in VRD Fuels

| 1 Пределы выкипания, град. | 2 Содержание меркаптановой серы в исходном топливе, % | 3 Содержание меркаптановой серы после испытаний, % | 4 Коррозия меди, г/м² |
|---|---|---|---|
| 60—130 | 0,001 | 5 Отсутствует | 0,5 |
| | 0,005 | » | 2,8 |
| | 0,015 | » | 7,6 |
| | 0,025 | » | 10,6 |
| | 0,045 | 0,015 | 14,9 |
| 130—240 | 0,001 | 5 Отсутствует | 0,4 |
| | 0,005 | 0,003 | 0,4 |
| | 0,015 | 0,012 | 1,5 |
| | 0,025 | 0,017 | 1,8 |
| | 0,045 | — | 3,1 |

1) Distillation range, degrees; 2) mercaptan sulfur content in initial fuel, %; 3) mercaptan sulfur content after testing, %; 4) copper corrosion, $g/m^2$; 5) none.

tained in the fuel can react in this period of time. Mercaptans vanish completely from these fuels when in contact with VB-24 bronze only after 150-200 hr. After this, the fuel is not able to corrode nonferrous metals. Consequently, the general regular course of the corrosion process in sulfurous fuels can be expressed by the curve shown in Fig. 199.

The mercaptans present in TS-1 and T-2 fuels possess various degrees of corrosion aggressiveness. It is clear from the data of Table 163 that the corrosion aggressiveness of the 130-240° fraction is considerably less than that of the 60-130° fraction, for this same mercaptan content.

When the 200-300° fraction was studied, despite its high mercaptan sulfur content (0.137%), corrosion of VB-24 bronze at a temperature of 120° did not occur. Consequently, as the distillation temperature of the mercaptans increases, their corrosion aggressiveness drops. In this connection, the mercaptans of the gas-oil fractions can be classified as neutral sulfur compounds.

The corrosion aggressiveness of VRD-fuel mercaptans depends not only upon the distillation temperatures, but also upon the chemical structure. Ya.B. Chertkov, V.N. Zrelov, and V.M. Shchagin [16] have studied the corrosion aggressiveness of mercaptans in the aliphatic and aromatic series. The results of the studies, shown in Table 164, indicate that the greatest corrosion ability is possessed by mercaptans of aliphatic structure, and the least by the aromatic mercaptans in which the thiol radical is attached directly to the ring. The aromatic mercaptans, in which the thiol radical occurs in side chains occupies an intermediate position.

As a consequence, the corrosion aggressiveness of fuels will depend upon the chemical structure of the mercaptans present in them. In

straight-distilled fuels of the TS-1 and T-2 types, the mercaptans present are chiefly of aliphatic structure and possess high corrosion aggressiveness, while the cracked fuels have mercaptans of aromatic structure with thiol radical attached to the aromatic ring [9].

In fuels formed by blending straight-run and cracked distillates, mercaptans from both groups may be present. The corrosion aggressiveness of such a blended fuel will depend upon the relationship between the aliphatic and aromatic mercaptans.

Ya.B. Chertkov, V.N. Zrelov, and R.D. Obolentsev [17] have studied the effect upon corrosion of VB-24 and VB-24N bronzes at temperatures of 120 and 150° of individual sulfur compounds (sulfides, thiophanes, and thiophenes). Sulfur compounds that could occur in VRD fuels were taken for the study. The results of the investigation showed that the thiophanes, dibenzothiophenes, and the majority of sulfides caused no noticeable bronze corrosion at 120 or 150°. Dibenzyl sulfide and methyl benzyl sulfide form an exception. At temperatures of 150°, these compounds cause corrosion of VB-24N bronze, and form deposits on its surface. This fact indicates that at a temperature of 150° these compounds break down and form corrosively active compounds. A similar picture is observed when the corrosion activity of type T-5 fuel with an increased sulfur content (1.42%) is studied. At a temperature of 120°, this fuel does not corrode bronze, while at a temperature of 150°, owing to the decomposition of certain sulfur compounds, considerable corrosion does occur, accompanied by the formation of copious corrosion deposits.

Corrosion of VRD fuel-apparatus parts manufactured from copper alloys depends not only upon the presence of mercaptans in the fuel, but also upon the composition of the fuel's content of oxygen, resinous, nitrogen, and other compounds. The removal of oxygen and res-

TABLE 164

Corrosion Activity of Mercaptans of Various Chemical structures

| 1 Меркаптаны | | Коррозия, 4 г/м² | Отложения на бронзе, 5 г/м² | 6 Поверхность бронзы |
|---|---|---|---|---|
| 2 концентрация в уайтспирите, % | 3 формула | | | |
| 7 Уайтспирит без меркаптанов | — | 0 | 0 | |
| 8 Нонилмеркаптан, 0,045 | $CH_3(CH_2)_8SH$ | 2,6 | 8,2 | |
| 9 Децилмеркаптан, 0,045 | $CH_3(CH_2)_9CH_2SH$ | 2,3 | 6,3 | |
| 10 Фенилэтилмеркаптан, 0,045 | | 2,2 | 5,0 | |
| 11 Бензилмеркаптан, 0,045 | | 1,9 | 4,3 | |

TABLE 164 (continued)

| | | | | |
|---|---|---|---|---|
| 12 Тиофенол, 0,530 | | 0,8 | 1,5 | |
| 13 α-Тионафтол, 0,530 | | 0,2 | 0 | |
| 14 Дитиорезорцин, 0,530 | | 0 | 0 | |

1) Mercaptans; 2) concentration in white spirit; %; 3) formula; 4) corrosion, $g/m^2$; 5) deposits on bronze, $g/m^2$; 6) bronze surface; 7) white spirit without mercaptans; 8) nonylmercaptan, 0.045; 9) decylmercaptan, 0.045; 10) phenyl ethyl mercaptan, 0.045; 11) benzylmercaptan, 0.045; 12) thiophenol, 0.530; 13) α-thionaphthol, 0.530; 14) dithioresorcin, 0.530.

inous compounds from fuels with elevated mercaptan content leads to an increase in the corrosion aggressiveness of that fuel. The oxygen and resinous compounds contained in fuels produced by thermal cracking have a good influence. The addition of these compounds to TS-1 fuel containing 0.047% mercaptan sulfur sharply decreases its corrosion aggressiveness [16]. In the absence of oxygen and resinous compounds, the surface of the bronze is coated with a gold film that protects the bronze from corrosion and prevents the formation of corrosion deposit. on its surface.

TABLE 165

Effect of Additives (0.05% Concentration) on Corrosion Aggressiveness of TS-1 and T-2 Fuels with Increased Mercaptan Sulfur Content (0.05%)

| 1 Присадки | 3 ТС-1 | | | T-2 | | |
|---|---|---|---|---|---|---|
| | 2 коррозия, г/м² | 3 отложения, г/м² | 4 осадки, мг/100 мл | 5 коррозия, г/м² | 6 отложения, г/м² | 7 осадки, мг/100 мл |
| 15 Исходное топливо . . . | 8,1 | 1,1 | 5,4 | 7,5 | 1,2 | 4,2 |
| | 8 Алифатические моноамины | | | | | |
| 16 Октадециламин . . . . | 7,5 | 0,5 | 3,0 | 8,7 | 0,7 | 2,8 |
| 17 Диоктадециламин . . . | 7,4 | 0,5 | 5,2 | 7,2 | 0,5 | 9,8 |
| | 9 Алифатические ди- и полиамины | | | | | |
| 18 Гексаметилендиамин | 2,1 | 2,7 | 16,1 | 1,0 | 3,2 | 1,7 |
| 19 Диэтилентриамин . . . | 7,7 | 0,6 | 6,9 | 9,3 | 1,1 | 6,4 |
| 20 Тетраэтиленпентаамин | 7,7 | 0,9 | 52,0 | 7,2 | 1,1 | 41,1 |
| | 10 Первичные ароматические моноамины | | | | | |
| 21 п-Гексиланилин . . . | 8,1 | 0,2 | 22,6 | 7,5 | 0,6 | 17,3 |
| 22 α-Нафтиламин . . . . | 7,2 | 0,5 | 21,2 | 6,8 | 0,7 | 18,1 |
| | 11 Вторичные ароматические моноамины | | | | | |
| 23 Дифениламин . . . . | 8,2 | 0,5 | 22,0 | 7,1 | 0,6 | 3,5 |
| 24 Фенил-α-нафтиламин | 8,5 | 0,9 | 1,3 | 7,6 | 1,2 | 2,5 |
| | 12 Третичные ароматические амины | | | | | |
| 25 Диметиланилин . . . . | 8,9 | 0,4 | 0,7 | 8,3 | 0,7 | отс. |
| 26 Диэтиланилин . . . . | 7,6 | 0,1 | 1,8 | 6,6 | 0,3 | 0,4 |
| | 13 Первичные ароматические диамины | | | | | |
| 27 α-Фенилендиамин . . . | 7,1 | 0,3 | 19,3 | — | — | — |
| 28 Бензидин . . . . . | 2,3 | 0,2 | 17,8 | — | — | — |
| | 14 Имидазолины | | | | | |
| 29 2-алкил ($C_9$—$C_{11}$) имидазолин . . . . . | 1,2 | 0,2 | 9,5 | — | — | — |
| 30 1,4-диимидазолилбутан | 6,7 | 0,9 | 1,2 | — | — | — |

1) Additives; 2) corrosion, g/m$^2$; 3) deposits, g/m$^2$; 4) sediments, mg/100 ml; 5) corrosion, g/m$^2$; 6) deposits, g/m$^2$; 7) sediments, mg/100 ml; 8) aliphatic monoamines; 9) aliphatic di- and polyamines; 10) primary aromatic monoamines; 11) secondary aromatic monoamines; 12) tertiary aromatic amines; 13) primary aromatic diamines; 14) imidazolines; 15) initial fuel; 16) octadecylamine; 17) dioctadecylamine; 18) hexamethylene diamine; 19) diethylene triamine; 20) tetraethylene pentamine; 21) n-hexylamine; 22) α-naphthyl amine; 23) diphenyl amine; 24) phenyl-α-naphthyl amine; [Key continued on next page]

[Key to Table 165 continued]: 25) dimethyl amine; 26) diethyl aniline; 27) α-phenylene diamine; 28) benzidine; 29) 2-alkyl ($C_9$-$C_{12}$) imidazoline; 30) 1,4-diimidazolyl butane; 31) TS-1.

The factor responsible for the corrosion-inhibiting effect of oxygen and resinous compounds in cracked kerosenes is their content of combined sulfur- and nitrogen-substituted heterocyclic compounds. Investigation of similar compounds of the tetrazole and pyrazoline types has shown that some of them such as 1-phenyl-5-mercaptan tetrazole and 1-thiocarbamide-3,5,5-trimethyl pyrazoline are effective corrosion-inhibiting additives which sharply reduce the corrosion aggressiveness of fuels with elevated mercaptan contents.

In the presence of these compounds, a protective film is formed on the bronze surface that protects the metal against corrosion. This property is possessed by compounds containing nitrogen and sulfur simultaneously: pyrazolines containing nitrogen alone, such as 4-amino-1-phenyl pyrazoline are not corrosion inhibitors.

In addition to these compounds, investigations were made of organic nitrogen compounds in the group of nitrogenous bases belonging to the aliphatic mono- and polyamines, the aromatic mono- and diamines, as well as heterocyclic compounds of the imidazoline type [18]. Investigation has shown (Table 165) that hexamethylene diamine, benzidine, and 2-alkyl ($C_9$-$C_{12}$)-imidazoline are extremely effective corrosion inhibitors for TS-1 and T-2 fuels with increased mercaptan-sulfur contents (0.05%).

It was established in the study of binary mixtures of nitrogen-containing compounds that the corrosion-inhibiting effect of the compounds mentioned above is increased in the majority of cases in the presence of several nitrogenous bases, with the exception of phenyl-α-naphthylamine which completely passivates the corrosion-inhibiting effect of the compounds.

Corrosion of VRD fuel-unit parts depends not only upon the presence of corrosion-active sulfur compounds in the fuel, but also upon the chemical composition of the alloys from which these parts are made. A study of the corrosion of bronze having various chemical compositions under the influence of TS-1 and T-2 fuels with increased mercaptan contents made it possible to establish that an increase of the amount of such components as aluminum, iron, and especially nickel or zinc contained in the bronze sharply increases its corrosion stability.

Consequently, in using fuels made from sulfurous petroleums, corrosion of parts made from nonferrous metals and their alloys in the VRD fuel system can be prevented by removing the corrosion-active sulfur compounds from the fuels, by employing corrosion-inhibiting additives, and by selecting an alloy chemical composition that will provide corrosion stability.

Corrosion Aggressiveness of Fuels Containing Water

The electrochemical corrosion of VRD fuel-system elements is observed when water gets into these units in the form of an individual phase. Water gets into an engine fuel system owing to the fact that kerosene and wide-boiling fuel types tend to absorb moisture from the surrounding atmosphere. The more aromatic hydrocarbons contained in the fuel and the greater the humidity and temperature of the outside air, the more water the fuel will absorb from the air.

If an aircraft carrying fuel stays on the ground for some time, water vapor will penetrate the fuel tanks through the vents. With the coming of night, and the drop in ambient temperature, the water vapors will cool and condense on the fuel-tank walls in the form of water drops in summer or frost in winter. Frost on fuel-tank walls can easily be observed in winter by opening the tank vent and looking in af-

ter the air temperature has dropped. The ice crystals or water drops that form drop into the fuel, partly dissolve in it, and partly are precipitated on fuel-tank sediment traps. The less fuel in the tanks and the longer the airplane stays on the ground, the greater the amount of water getting into the aircraft fuel system.

When the engine is started, the water enters the ducts and is carried along by the stream of fuel through the entire fuel system, accumulating in the fuel elements and at bends in the ducts. This water, after being enriched by corrosion-active sulfur, oxygen, and other compounds from the fuel, rapidly corrodes fuel-unit parts made from various grades of steel. Such corrosion frequently causes serious disturbances in operation for even failure of the fuel units. Thus, G. Shashkov [19] states that in aircraft operation it is frequently necessary to contend with engine malfunctions caused by the corrosive action of moisture on fuel-system elements. The water, getting into the fuel pump, corrodes pistons, sometimes causing them to seize and bring the fuel pump to a halt. In this case, the inclined washer of the fuel pump may be liable to considerable damage. There is also frequently corrosion of pist ns and rod of the fuel-pump servo-piston, the race of the inner ring, and the pins in the combination fuel-pump bearing, the working surface of the governor valve, the inside surface of the fuel-pump sphere bearing, the side surface of the governor-valve lever axle, the rod and eccentric ring of the barometric regulator, the automatic fuel-distribution stop-valve sleeve, the mixer disk, the mixer, the mixer socket, valve seat and gear axle for the throttle-valve lever, the low-throttle needle, etc.

As a rule, it is primarily the rubbing parts of fuel apparatus moving with intermittent or low speeds that are liable to corrosion.

Fuel-system element parts are made from various alloy steels. The

surfaces of these parts are subject to heat treatment and chemical treatment (hardening, carburizing, nitriding, etc.) that result in the formation of special protective layers on the part surfaces; they have a substantial effect upon the corrosion stability of steel parts.

The corrosion of low-alloy steels in the presence of moisture is accompanied by the formation of quantities of finely dispersed brown suspended matter, chiefly oxides of iron. This suspended matter easily gets into the fuel, owing to its great density, and clogs filtering elements and precision mating parts. In the latter case, these deposits may act as abrasives, increasing wear above permissible standards.

Viscosity Properties of VRD Fuels

One of the most important conditions for normal operation of a VRD combustion chamber is the degree of fuel dispersion. The majority of modern VRD employ a whirlpool-type nozzle to disperse the fuel. Such a nozzle has a swirl chamber in which the fuel is supplied through tangentially arranged apertures. As a result, the fuel eddies in the chamber and arrives at the outlet aperture in the form of a stream, within which there is a core of air. The fuel stream leaves the output aperture of the nozzle in the form of a hollow cone (Fig. 200), with a vertex angle of about $90^{\circ}$ [20]. In addition to structural peculiarities, the degree of dispersion is greatly affected by the surface tension and viscosity of the fuel; the fuel viscosity is of the greatest importance. The pumping of fuel from the fuel tanks to the combustion chamber and the operation of the fuel-regulating apparatus also depends upon the fuel viscosity. In order to provide the required degree of dispersion, the upper limit placed on fuel viscosity should equal no more than 6-10 centistokes at a temperature of $-40^{\circ}$. In order to provide reliable pumpability in a VRD fuel system, the fuel viscosity should not exceed 60 centistokes at a temperature of $-40^{\circ}$. When

these limits are exceeded, it is necessary to employ special, more efficient nozzles, more powerful pumps, or the fuel must be heated.

Fig. 200. Photograph showing stream of fuel dispersed by whirlpool nozzle.

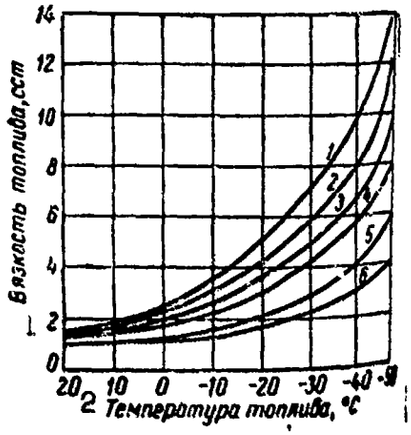



Fig. 201. VRD fuel viscosity as a function of temperature. 1) T-1 fuel; 2) type JP = 1 Danish fuel; 3) type JP = 1 English fuel; 4) TS-1 fuel; 5) TS-2 fuel; 6) type JP = 4 Swedish fuel; 7) fuel viscosity, centistokes; 8) fuel temperature, °C.

Study of fuel-viscosity variations as a function of temperature show that modern VRD fuels up to kerosene grade inclusively have the necessary viscosity values for any working temperatures down to $-40^{\circ}$ (Fig. 201). At present, however, a tendency is visible to use heavier gas-oil type fuels for VRD. Such fuels do not possess the required viscosity-temperature characteristics. Thus, their viscosity at $-40^{\circ}$ is considerably greater than 60 centistokes, which greatly complicates their utilization.

The basic types of hydrocarbons contained in VRD fuels possess nearly identical viscosity at $20^{\circ}$ [21, 22, 23]. An exception is formed by the bicyclic hydrocarbons whose viscosity, as a rule, is greater than the viscosity of other classes of hydrocarbons with the same boiling point. As the boiling point increases, the viscosity of all hydrocarbon groups rises. Thus, where the boiling point of the hydrocarbons rises from 100 to $300^{\circ}$, the viscosity increases from 0.005 to 0.05 poise. As Fig. 202 shows, a sharp rise in viscosity is observed for hydrocarbons that boil at temperatures above $200^{\circ}$.

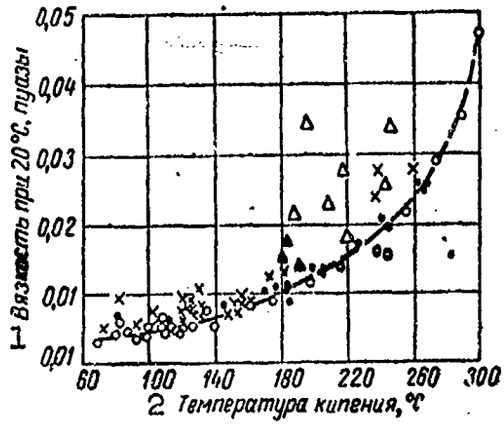



Fig. 202. Viscosity-temperature curve for VRD-fuel hydrocarbons in accordance with their structure and boiling point. O) Paraffins; X) naphthenes; ●) monocyclic aromatic hydrocarbons; Δ) bicyclic aromatic hydrocarbons. 1) Viscosity at 20°C, poises; 2) boiling point, °C.

Ya.B. Chertkov, K.I. Klimov, and V.N. Zrelov [22] have investigated the viscosity properties at low temperature of hydrocarbons having the same chemical composition, isolated from 50-degree fractions of T-1, TS-1, and T-2 fuels. The investigation showed that hydrocarbons boiling at up to 200° have viscosities at a temperature of —40° lower than 10 centistokes, which provide satisfactory fuel dispersion under working conditions. Hydrocarbons that boil above 200° have viscosities greater than 10 centistokes. Combinations of hydrocarbons boiling up to 200° and at 200-350° will produce a fuel having the required viscosity at —40°C.

CARBON-FORMING CAPABILITY OF VRD FUELS

Under operating conditions in a jet engine, carbon deposits are observed.

When a VRD is operated with commercial T-1, TS-1, and T-2 fuels, the amount of carbon that forms in the combustion chambers is slight and normally has no negative effect upon engine operation. At the present time, however, the problem of carbon formation in VRD looms large

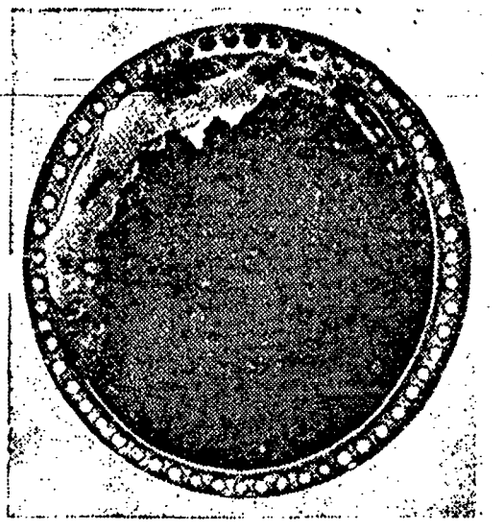


Fig. 203. Deposit of carbon in TRD combustion chamber (aircraft flying at altitude of 9 km for 20 hr, wide-boiling type fuel used).

TABLE 166

Increase in Carbon Deposited in TRD Combustion Chamber Using T-1 Fuel

| 1 Места отложений нагаров | 2 Количество нагара (в г) за | | | | |
|---|---|---|---|---|---|
| | 20 час. | 40 час. | 60 час. | 80 час. | 100 час. |
| | 7 | 7 | 7 | 7 | 7 |
| 3 Двигатель РД-45: | | | | | |
| 4 на жаровых трубах . . . | 1,0 | 2,0 | 3,5 | 7,5 | — |
| 5 на форсунках . . . . . | 0,1 | 0,2 | 0,3 | 0,4 | 0,5 |
| 6 Двигатель ВК-1: | | | | | |
| 4 на жаровых трубах . . . | 0,8 | 1,5 | 2,5 | 4,0 | 6,3 |
| 5 на форсунках . . . . . | 0,2 | 0,3 | 0,4 | 0,5 | 0,6 |

1) Point of deposition of carbon; 2) amount of carbon (g) after; 3) RD-45 engine; 4) at fire tubes; 5) at nozzle; 6) VK-1 engine; 7) hours.

in connection with the tendency toward employing heavier gas-oil type fuels in VRD. These fuels contain a considerable quantity of bi- and tricyclic aromatic hydrocarbons that have a greater tendency toward carbon formation.

Soot-type and coke-type carbon deposits are encountered. Deposits are formed on the fire-tube walls in the combustion chamber (Fig. 203), on the nozzles (Fig. 204), and on the plugs. In engines using prelim-

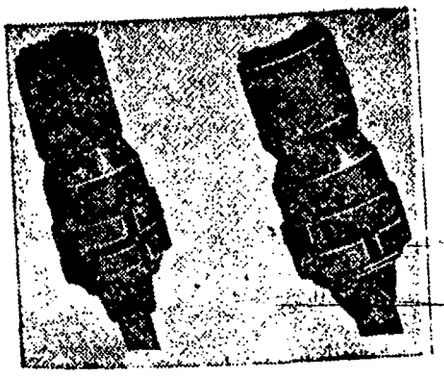


Fig. 204. Carbon deposits on fuel nozzles of TRD operating with T-1 fuel.

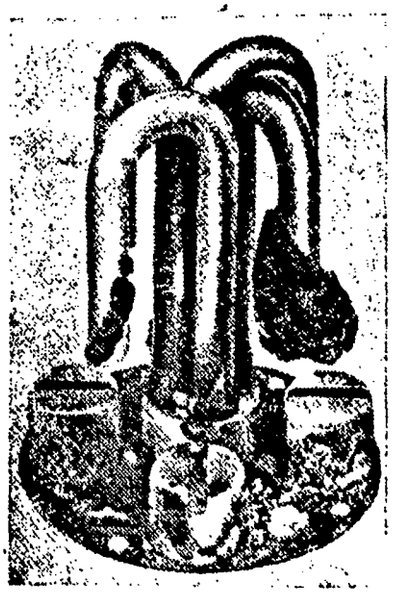


Fig. 205. Formation of carbon on vaporizer of TRD (aircraft flying at altitude of 6 km for 6 hr, gas-oil type fuel).

inary fuel vaporization, carbon is deposited on the vaporizer (Fig. 205) [24].

The amount of carbon deposited increases with the engine operating time, as Table 166 shows. The rate of carbon formation on nozzles remains constant in time, while at the fire-tube walls, the carbon is first deposited at a constant rate, and then after 50 hrs of operation, the rate of carbon deposition rises sharply.

When finely dispersed fuel is burned, the carbon is deposited in zones near the nozzle. With rough dispersion, the carbon is deposited near the combustion-chamber outlet, i.e., as the drop size of the dispersed fuel increases, the carbon-formation zone shifts toward the combustion-chamber outlet.

The amount of carbon formed decreases for a more finely dispersed fuel. Thus, a fuel containing 90% aromatic hydrocarbons produces 650 times more carbon when used with a nozzle having a flow number of 1.65 (large drops) than with a nozzle having a flow number of 0.9 (fine drops) [20].

**Carbon deposited on fuel nozzles impairs fuel dispersion, distorts** the flame front and structure, and also impairs fuel combustion.

Distortion of flame structure and form in turn may cause the flame to shift, leading to deposition of carbon on the fire-tube walls. As a

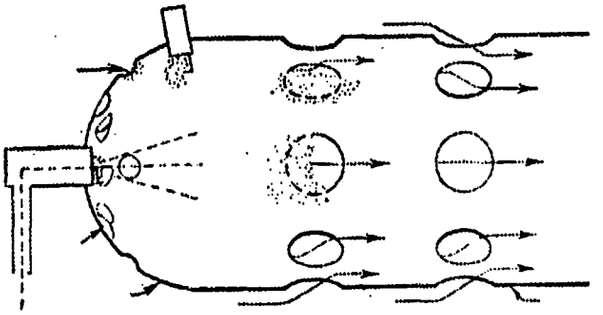


Fig. 206. Diagram showing deposition of carbon in TRD combustion chamber.

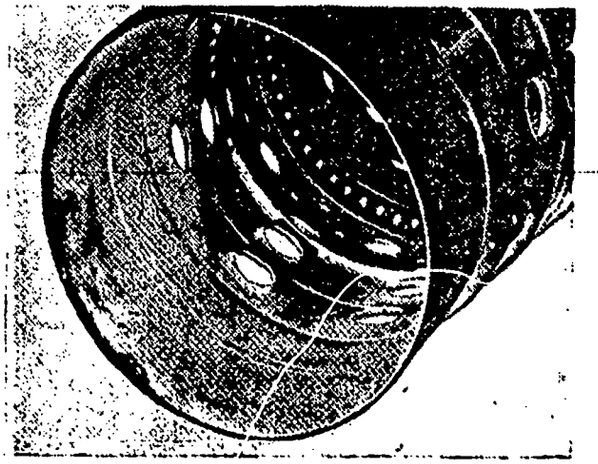


Fig. 207. Buckling and cracking of VRD flame tube.

rule, as Fig. 206 shows, carbon is deposited in the inlet zone of the primary-air chamber around holes designed for this purpose [15]. The carbon deposited in this zone is of the coke type, and it sometimes reaches 3-4 cm in thickness.

The appearance of local carbon deposits on the fire tubes creates a large local temperature gradient on their walls, leading to the formation of local stresses; this may cause buckling, and sometimes even cracking of the fire-tube walls (Fig. 207).

Noticeable buckling of fire tubes is also seen in tests of a fuel with high carbon-forming ability after a 30-hr flight [5].

While the chamber is in operation, pieces of the carbon depos[illegible]

may break loose from the walls and, passing into the gas turbine, can block the turbine nozzles and erode the turbine blades.

The structure of the gas flow in the combustion chamber has a considerable effect upon the carbon-forming ability of a fuel. If a special air stream is directed along the fire-tube walls, there will be a sharp decrease in the amount of carbon deposited upon the combustion-chamber walls. This has been confirmed experimentally on a small-scale TRD chamber; the results are shown below.

| 1 Отложения нагара | 2 Количество нагара (в г) за | | | | |
|---|---|---|---|---|---|
| | 25 мин. | 50 мин. | 75 мин. | 100 мин. | 125 мин. |
| | 3 | 3 | 3 | 3 | 3 |
| 4 Без потока воздуха вдоль стенок . . . . . | 5 | 25 | 75 | 110 | 140 |
| 5 С потоком воздуха вдоль стенок . . . . . | 0 | 2 | 5 | 15 | 25 |

1) Carbon deposit; 2) amount of carbon (g) after; 3) minutes; 4) no air flow along walls; 5) with air flow along walls.

This measure is one of the most important steps that can be taken to avoid carbon deposition on combustion-chamber walls.

The following factors affect the formation of carbon in fire tubes:

1) the ratio of the weights of air and fuel in the primary combustion zone;

2) the dynamic pressure of the entering air;

3) the degree of dispersion of the fuel;

4) the structure of the gas flow in the primary combustion zone;

5) the temperature of the fire-tube walls;

6) the chemical composition of the fuel.

The structure of the carbon makes it possible to form an opinion as to the factors responsible for the carbon deposition. If the deposit has the structure of amorphous carbon which, as we know, forms at low pressures and temperatures with an excess of oxygen, the factor

causing carbon to be deposited will be found in an imperfect cycle and the engine design. Such a pattern was observed in the first models of air-reaction engines. In modern TRD, carbon comes in the form of pure graphite-type carbon. This indicates that the cause for formation of the carbon is not poor organization of the combustion cycle but the chemical composition of the fuel.

Evaluating the Carbon-Forming Ability of a Fuel

In order to evaluate the carbon-forming ability of fuels in a full-sized engine, it is necessary to use considerable fuel and a large

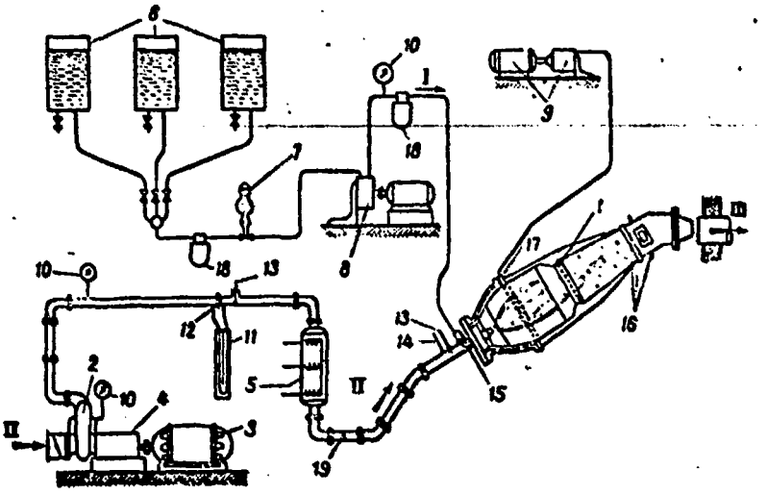


Fig. 208. Diagram showing single-chamber installation for evaluating carbon-forming capability of VRD fuels. 1) Combustion chamber; 2) force pump; 3) electric motor; 4) reducer; 5) electric heater; 6) fuel tanks; 7) sample take-off; 8) fuel pump; 9) magneto; 10) pressure gauge; 11) differential manometer; 12) nozzle; 13) thermometer; 14) temperature regulator; 15) nozzle; 16) thermocouples; 17) spark plug; 18) filter; 19) throttle valve. I) Fuel; II) air; III) gases in atmosphere.

amount of time. Thus, there is a present tendency toward creating small laboratory devices and installations that make it possible to evaluate carbon-forming ability with a small quantity of fuel within a short period of time. These installations sometimes resemble in their dimensions the widely known single-cylinder installations used to determine

the antiknock properties of gasoline; sometimes they take the form of small glass laboratory devices.

Single-chamber installations for determining the carbon-forming ability of fuels were developed by Ye.R. Tereshchenko (Fig. 208) [26] and by Williams [27]. As a rule, a single-chamber installation consists of a small-scale combustion chamber, an air compressor, a system for metering and supplying fuel, and accessories used to analyze the exhaust gases. The carbon-forming ability of a fuel is evaluated either on the basis of an analysis of the exhaust gases and a determination of their carbon content, or on the basis of a quantitative measurement of the carbon deposited on the flame-tube walls by weighing the chamber before and after a specified test period.

Some of these installations make it possible to adjust and measure the primary and secondary air separately, and also permit regulation of the flame-tube wall temperature. By changing the conditions mentioned above, it is possible to investigate the effect of several operating factors upon carbon formation, and the influence of the carbon-forming ability of the fuel on various operating regimes.

The fuel flow rate amounts to about 20-50 liter/hr for such installations, and the test time to 1 hr.

Ya.B. Chertkov, V.N. Zrelov, and I.V. Kalechits [28] have developed a laboratory device and a method for determining the carbon-forming ability of fuels.

The carbon-forming ability of a fuel is found by this method for various combustion regimes characterized by the excess-air factor which ranges from 0.5 to 4.5. The carbon-forming ability is expressed in milligrams of carbon per milliliter of fuel.

A series of determinations of fuel carbon-forming ability for various excess-air coefficients should take no more than 30 min. One

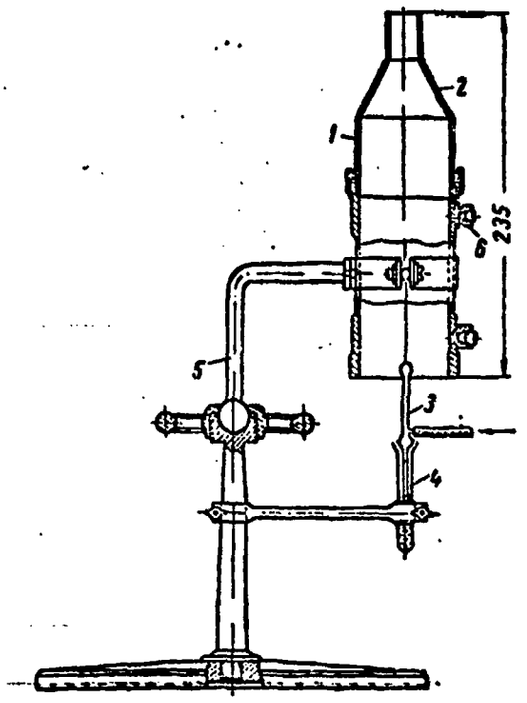



Fig. 209. Laboratory device for determining the gum-forming ability of VRD fuels. 1) Cylindrical section of combustion chamber; 2) nozzle section of combustion chamber; 3) pneumatic nozzle; 4) vessel with fuel; 5) stand; 6) gas exit hole.

determination should consume 1-3 ml of fuel.

The instrument, together with the method, permits a rapid determination under laboratory conditions of fuel gum-forming capability, using small amounts of fuel. This method estimates the total carbon-forming ability of the fuel.

There exist instruments and methods for evaluating the partial carbon-forming ability of a fuel according to the formation of carbon on the fire-tube walls [29]. Figure 209 shows a diagram for a laboratory device used to evaluate the carbon-forming ability, developed by Ya.M. Paushkin and associates [30]. The device consists of a straight-through flow combustion chamber having cylindrical and conical nozzle sections. When 2-3 g of fuel is burned, carbon is deposited in the noz-

zle section of the combustion chamber. The amount of carbon is determined by weighing the nozzle section of the combustion chamber.

A lamp that is also widely employed to determine the properties of illuminating kerosenes [31] is used in the United States and England for determining the carbon-forming ability of VRD fuels. The carbon-forming ability of VRD fuels is determined on this device according to the so-called smoke point. The smoke point is the maximum length of the flame at the instant smoke appears, and it is expressed in millimeters. The choice of the smoke point for characterizing the carbon-forming ability of VRD fuels is based upon the fact that there is a relationship, discussed below [24] between the smoke point and the deposition of carbon in a VRD combustion chamber.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1Точка дымления, мм . . . . | 12 | 18 | 21 | 23 | 26 | 30 | 43 |
| 2Количество нагара, г . . . . | 7,5 | 4,8 | 3,2 | 1,8 | 1,6 | 0,5 | 0,4 |

1) Smoke point, mm; 2) quantity of carbon, g.

The smoke point is used to evaluate the carbon-forming abilities of kerosene-type fuels.

The smoke point is presently given in the specification for JP-5 fuel. It should be less than 20 mm in value.

The volatility is important in evaluating the carbon-forming ability of wide-boiling fuels. Thus the carbon-forming ability of these fuels is determined in accordance with the carbon-formation index, which connects the smoke point and the fuel volatility characteristic. The carbon-formation index equals the smoke point plus 0.42% of the distillate up to 204°. Tests have shown that there is a relationship between the carbon-formation index and the amount of carbon in an engine, as we can see from the figures given below.

| 1 Индекс нагарообразования . . | 13 | 17 | 25 | 42 | 45 | 65 | 66 |
|---|---|---|---|---|---|---|---|
| 2 Количество нагара, г . . . . | 4,9 | 4,2 | 3,8 | 3,2 | 1,9 | 1,0 | 0,5 |

1) Carbon-formation index; 2) quantity of carbon, g.

The carbon-formation index, as in the case of the smoke point, is included in the specification for JP-5 jet fuels; it has recently been established, however, that the smoke point is a more objective measure of the carbon-forming ability of such fuels [31]. The magnitude of the carbon-formation index for JP-5 fuel should be at least 54.

It follows from the data given that the methods most commonly used abroad to find the carbon-forming ability of commercial VRD fuels under laboratory conditions are based upon a determination of the smoke point in the lamp mentioned above.

Effect of Fuel Quality on Carbon Formation

The basic characteristic that has a considerable influence on the carbon-forming capability of a fuel is the group chemical composition. In order to determine the carbon-forming capability of the hydrocarbons comprising TRD fuels, Baku T-1 fuel was separated by chromatography on silica gel into methane-naphthene, monocyclic aromatic, and bicyclic aromatic hydrocarbons. Their carbon-forming ability was studied (Fig. 210).

The hydrocarbons can be arranged in the following order with respect to their carbon-forming ability: paraffin → naphthene → monocyclic aromatic → bicyclic aromatic hydrocarbons.

In addition to chemical composition, volatility has a great influence upon the carbon-forming ability. Hydrocarbons and fuels that differ in volatility and chemical composition may be arranged as shown in Fig. 211 in accordance with their carbon-forming ability.

Here the oblique lines mark off the specimens of the paraffin,

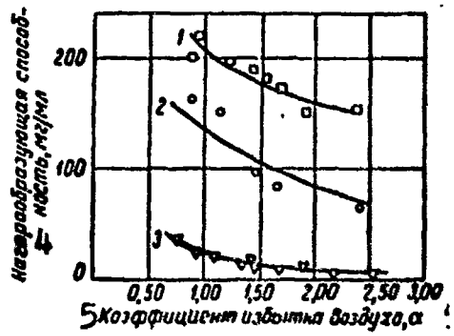



Fig. 210. Carbon-forming ability of hydrocarbons in Baku T-1 fuel. 1) Bicyclic aromatic hydrocarbons; 2) monocyclic aromatic hydrocarbons; 3) methane-naphthene hydrocarbons; 4) carbon-forming ability, mg/ml; 5) excess-air factor, α.

naphthene, and aromatic series. The slope of these curves shows that within series, the carbon-forming ability rises with decreasing volatility of the fuel. The aromatic hydrocarbons with side paraffin chains are characterized by lower carbon-forming capability than hydrocarbons without side chains. Thus, toluene, cumene, and amylbenzene are arranged within the diagram so as to qualitatively reflect their structure and volatility.

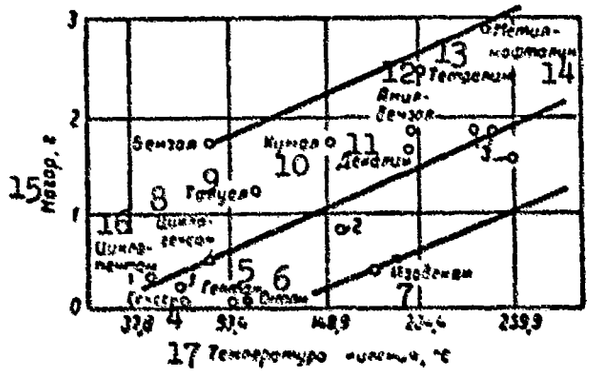



Fig. 211. Carbon-forming ability as a function of chemical composition and volatility. 1) Gasoline-type fuel; 2) kerosene-type fuel; 3) gas-oil type fuel; 4) hexene; 5) heptane; 6) octane; 7) isodecane; 8) cyclohexane; 9) toluene; 10) cumene; 11) decaline; 12) amylbenzene; 13) tetraline; 14) methylnaphthaline; 15) carbon, g; 16) cyclopentane; 17) boiling point, °C.

The carbon-forming ability of a fuel increases also as the end-point temperature goes up and as the fuel density rises [32].

The laws of carbon-forming ability for various classes of hydrocarbons established under laboratory conditions were verified by a se-

TABLE 167

Carbon-Forming Ability of Fuels of Various Chemical Compositions in a Full-Sized Engine

| 1 Топливо | 2 Химический состав, % | | | 6 Нагарообразующая способность, % |
|---|---|---|---|---|
| | 3 ароматические | 4 нафтеновые | 5 парафиновые | |
| 7 Ароматическое . . . . | 75,2 | 11,4 | 13.4 | 700 |
| 8 Нафтеновое . . . . . | 1,4 | 51,9 | 46,7 | 70 |
| 9 Парафиновое . . . . . | 2,6 | 5,2 | 92,2 | 10 |
| 10 Стандартное . . . . . | 19,4 | 39,2 | 41,4 | 100 |

1) Fuel; 2) chemical composition, %; 3) aromatic; 4) naphthene; 5) paraffin; 6) carbon-forming ability, %; 7) aromatic; 8) naphthene; 9) paraffin; 10) standard.

ries of tests on a full-sized engine, using fuels differing sharply in chemical composition [33, 34]. The carbon-forming capability of the aromatic, naphthene, and paraffin fuels was compared with that for a standard fuel used in turbojet engines. The results of these tests (Table 167) indicate that the relationship between carbon-forming ability for a fuel and its chemical composition, established under laboratory conditions, is completely confirmed for the engine.

The flight tests also confirmed the high carbon-forming capability of the aromatic hydrocarbons; it was noted, however, that the bicyclic aromatic hydrocarbons had the basic influence on carbon-forming ability. Thus, in flight tests of a fuel containing a small amount of aromatic hydrocarbons with the major proportion formed by bicyclic aromatic hydrocarbons it was established that within only 4-7 hours of flight, the fuel nozzles and plugs were covered by so much carbon that in the case of a flameout, the combustion process could not have been reestablished; this would have inevitably led to an accident. In another test of this fuel, after a 30-hr flight, the amount of carbon had increased considerably even on the flame-tube walls [5].

In some combustion chambers, the carbon forming when bicyclic aromatic hydrocarbons are burned does not remain on the flame tubes, nc.

zles, and plugs. In this case, the carbon is carried out of the combustion chamber by the gas stream. In the meanwhile, cracking, buckling, and burnout of the flame tubes continues to occur. This is due to the fact that flame brightness increases sharply owing to the presence of fine carbon particles that are responsible for the radiation of an excessive flow of heat to the fire-tube walls; this increases their temperature.

The investigations of Droegemueller and Nelson [31] have shown that in order to eliminate this phenomenon in VRD fuels, no more than 3% of bicyclic aromatic hydrocarbons should be present.

Both fuel quality and engine operating conditions affect the carbon-forming ability of VRD fuels. Of the operating conditions, the most important are the temperature and pressure of the air supplied, the excess-air coefficient, and the distribution of air between the primary and secondary combustion zones.

The carbon-forming ability of VRD fuels having a high aromatic hydrocarbon and sulfur compound content can be decreased by using 0.1-5.0% peroxide and nitrate additives [35, 36]. Thus, if 2% cumene hydroperoxide is added to a fuel containing 99% aromatic hydrocarbons, carbon formation is more than halved. Ya.M. Paushkin and associates [30] have also shown that the carbon-forming ability of fuels with high contents of aromatic hydrocarbons may be decreased considerably by adding carbon-inhibiting additives.

With the aim of reducing VRD-fuel carbon-forming ability, Sacks and Ziebell [37] studied several halogen-derivative hydrocarbons as additives: carbon tetrachloride, n-propylchloride, n-propylbromide, n-butyliodate, etc. The investigation established that the halogen-derivative hydrocarbons did not depress the carbon-forming ability in concentrations of 1%, while in concentrations of 10%, several of them fa-

cilitated the formation of carbon.

High-Temperature Gas Corrosion

The corrosion of combustion-chamber walls, nozzles, and gas-turbine parts has been studied for fuels with various sulfur contents (from 0.2 to 1.5%). Nickel is the basic component contained in the heat-resistant alloys and steels from which the combustion chamber, gas turbine, and jet nozzle are made. Up to 80.0% nickel is contained in such alloys [6].

When all of the sulfur compounds in a fuel are burned, sulfur dioxide is formed. Under high-temperature conditions (above 1000°), nickel sulfide may form; this leads to the formation of a nickel-nickel sulfide eutectic. The melting point of this eutectic is roughly 650°, and this may cause rapid destruction of appropriate parts.

In modern VRD, however, the temperatures of the walls and parts of the combustion chamber, reaction nozzle, and gas turbine are low, and with a uniform flame do not exceed 800-900°.

Bench tests of German VRD have shown [39], that under such conditions when a fuel containing up to 1.5% sulfur is used, gas corrosion of elements in the gas-air system of the engine is not observed.

Metals contained in the fuels as ash can affect corrosion of VRD fire-tube walls, in addition to sulfur compounds. Actually, VRD fuels contain little ash, no more than 0.005%; the metals entering into the ash, however, acting as catalysts, facilitate the development of corrosion processes. Cases of fire-tube corrosion have been noted for certain grades of TS-1 fuel. T-1 fuel does not cause corrosion of VRD fire tubes.

The most active metals facilitating the development of corrosion processes in combustion chambers are vanadium and sodium. Ya.B. Cherkov, V.N. Zrelov, and N.I. Marinchenko [40] have carried out a spec-

TABLE 168

Composition of VRD Fuel Ash Residue (%)

| 1 Состав золы | 2 Т-1 стандартное | ТС-1 с 0,045% меркаптановой серы 3 | 4 ТС-1 стандартное | |
|---|---|---|---|---|
| | | | 5 образец 1 | 6 образец 2 |
| Cu | 10,0 | 45,5 | 1,0 | 13,0 |
| Fe | 11—20 | 2—6 | 30,0 | 10,0 |
| Zn | 3—10 | 3—10 | 20—30 | 1—3 |
| Pb | 1—3 | 1,0 | 0,4—1,0 | 0,4—1,0 |
| Mg | 1,0 | 0,1--0,3 | 0,1—0,3 | 1—2 |
| Al | 1—3 | 11,0 | 0,3 | 1,0 |
| Na | 1—3 | 1,0 | 0,4—1,0 | 11,0 |
| Cd | 1—3 | — | 1—3 | 10,0 |
| Si | 10,0 | 1—3 | 3—6 | 3—10 |
| Ca | 1,0 | 7 Следы | 0,3 | 1,0 |
| Sn | 1—3 | 0,4 | 0,3—1,0 | 10—15 |

1) Ash composition; 2) T-1, standard; 3) TS-1 with 0.045% mercaptan sulfur; 4) TS-1, standard; 5) specimen 1; 6) specimen 2; 7) traces.

investigation of the ash residues formed by TS-1 fuel. The results of this investigation are given in Table 168. It is clear from the data shown that the composition of ashes produced by T-1 and TS-1 fuels is exceptionally varied. Among the metals present in the greatest quantities are copper, iron, zinc, cadmium, and tin; these substances are normally not considered corrosive. These metals get into the fuel while it is being produced, transported, and pumped. The fuel is considerably enriched with metals while it is being pumped through the aircraft and engine fuel systems, which have parts made from nonferrous alloys.

Among the metals contained in T-1 and TS-1 fuels sodium is extremely corrosive. It enters the fuel at the refinery, where a solution of sodium hydroxide is used in alkali refining. Sodium salts of petroleum acids are removed from the fuel following alkali refining by scrubbing with water. If scrubbing is not carried out with sufficient care, the fuel will contain an increased amount of sodium in the form of salts of petroleum acids (see Table 168, fuel TS-1, specimen 2, whose ash contains 11.0% sodium).

The artificial addition of sodium naphthenates to a fuel causes increased combustion-chamber corrosion in gas turbines. Leoynd and Probert [41] showed that sodium pyrosulfite, vanadium pentoxide, and sodium vanadate cause vigorous gas corrosion developing specially intensively at high temperatures. An investigation of fuel containing 0.2% sulfur with added sodium chloride led to considerable corrosion; the corrosive deposits contained 95% sodium sulfate [42].

At present it is considered that vanadium and molybdenum can also affect corrosion of combustion-chamber walls; these metals are not found in T-1 and TS-1 fuels, however.

OXIDIZABILITY OF VRD FUELS UNDER STORAGE CONDITIONS

The oxidizability of VRD fuels under storage conditions depends basically upon the chemical composition of the fuel, as well as upon the method by which it is produced, refined, and upon the storage conditions themselves. An investigation of kerosene-type fuel oxidation under ambient-temperature conditions established that T-1 and TS-1 fuels obtained by straight distillation oxidized under these conditions with great difficulty, and the oxidation products accumulated very slowly in them. For kerosenes obtained by thermal cracking, the oxidation products accumulated rapidly. These kerosenes are relatively instable [44].

The stability of T-1, TS-1, and T-2 fuels depends upon the amount of unstable hydrocarbons present in them. Low-stability hydrocarbons in these fuels are monocyclic aromatic hydrocarbons with an unsaturated side chain [45].

Under storage conditions, these hydrocarbons do not oxidize at the double bond, with this bond breaking, as had been supposed previously, but at the C-H bond located in the β-position to the double bond, with the formation of hydroperoxides [46].

TABLE 169

Composition of Oxidation Products Formed upon Storage in Tuymazy Cracked Kerosene

| 1 Продукты окисления | 2 Содержание, % |
|---|---|
| 3 Спирты | 49.7 |
| 4 Соединения с карбонильной группой | 23.8 |
| 5 Эфиры | 19.8 |
| 6 Кислоты | 5.8 |

1) Oxidation product; 2) content, %; 3) alcohol; 4) compounds with carbonyl radical; 5) esters; 6) acids.

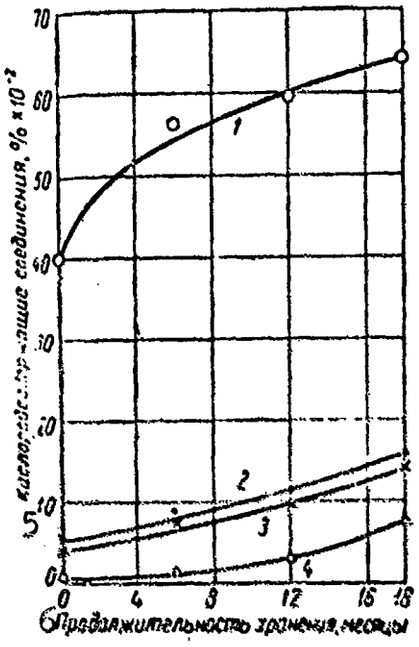



Fig. 212. Variation in oxygen-compound content during storage of sulfurous fuel containing cracked components. 1) Alcohol; 2) compounds with carbonyl radical; 3) esters; 4) acids; 5) oxygen-containing compounds, % x $10^{-2}$; 6) length of storage, mos.

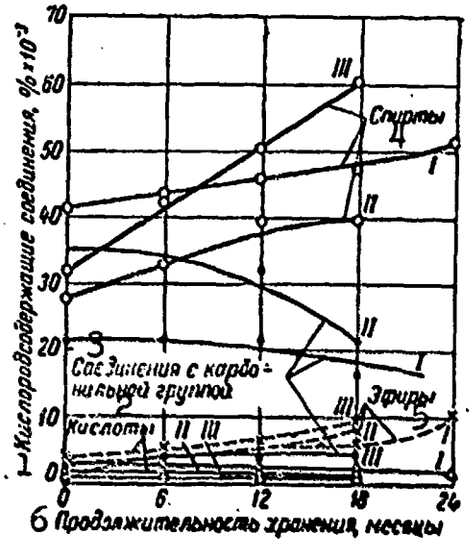



Fig. 213. Variation in oxygen compound content during storage of VRD fuels. I) Baku T-1; II) Groznyy T-1; III) TS-1. 1) Oxygen-containing compounds, % x x $10^{-3}$; 2) acids; 3) compounds with carbonyl radical; 4) alcohol; 5) esters; 6) length of storage, months.

At normal ambient temperature, the decomposition of hydroperoxides is accompanied by the formation of a complex mixture of combustion

products. Among the combustion products, as Table 169 shows, alcohols are the most important (49.7%).

In certain cracked fuels, the alcohol content of the combustion products reaches 70%. The total amount of acids and compounds with a carbonyl group does not exceed 29.5%.

Observation of the accumulation of individual oxygen-compound groups in VRD fuels obtained by straight distillation and by thermal cracking has shown that the chief direction of the oxidation process during storage is the formation of alcohol (Fig. 212) [44]. The formation of acids and compounds with carbonyl groups is subsidiary in nature.

During fuel storage, the primary oxidation products forming as the result of hydroperoxide decomposition are liable to further transformation leading to the formation of resinous substances.

Thus, in the oxidation of Tuymazy cracked kerosene after six months of storage, the rate at which alcohol accumulates decreases. This is not due to any cessation in alcohol formation, but to the fact that the alcohols forming are rapidly converted to other substances.

In order to solve the problem of the conversions of alcohols as the chief oxidation-process products, a study was made of neutral resinous substances isolated from fuel-oxidation products and forming 95-97% of all resinous substances. The structure of the neutral resinous substances included two benzene rings, one hydroxyl radical, one unsaturated bond, two oxygen atoms; their molecular weight was twice as great as the mean molecular weight of the alcohols previously studied [47]. We may consequently assume that the neutral resinous substances are products of oxidative polymerization of alcohols. This is the chief manner in which resinous substances are formed in VRD fuels under storage conditions.

In T-1 and TS-1 straight-run fuels (Fig. 213) there is also a drop in the number of compounds with a carbonyl radical during storage. Compounds with a carbonyl radical, basically ketones, are subject to condensation accompanied by a drop in the amount of compounds with the carbonyl group; this leads to a sharp rise in the molecular weight and specific gravity of the oxidation products.

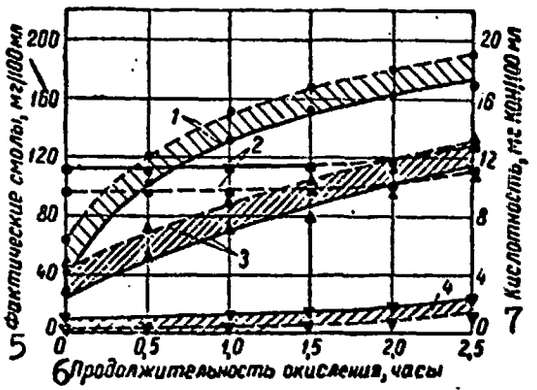



Fig. 214. Effect of hydroxy acids, acids, and neutral resins on the oxidizability of a sulfurous fuel with cracked components. 1) 297 mg/100 ml neutral gums; 2) 88 mg/100 ml neutral gums; 3) 6.6 mg/100 ml hydroxy acids; 4) initial fuel; 5) existent gum, mg/100 ml; 6) duration of oxidation, hours; 7) acidity, mg KOH/100 ml. —— Existent gum; --- acidity.

During storage, acids react with alcohols to form esters having a molecular weight twice as great as the molecular weight of the initial compounds. The esters formed are resinous in character and contain a single ester group and about 2 oxygen atoms.

At the same time, these acids are liable to further oxidation resulting in the formation of hydroxy acids which are dark viscous gummy substances. A study of the nature of the hydroxy acids has shown that they contain about 3 oxygen atoms and their molecular weight is greater than the molecular weight of the initial fuel hydrocarbons.

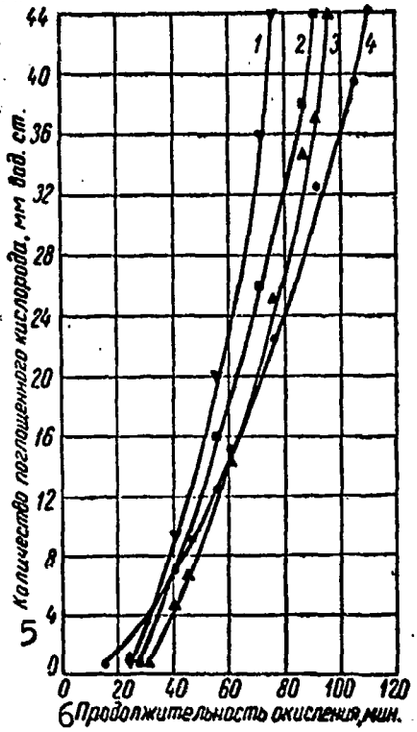



Fig. 215. Effect of phenyl compounds on oxidizability of Baku fuel with cracked components. Phenyl compounds added (%): 1) 0.065; 2) 0.035; 3) 0.016; 4) initial fuel. 5) Amount of oxygen absorbed, mm water; 6) duration of oxidation, min.

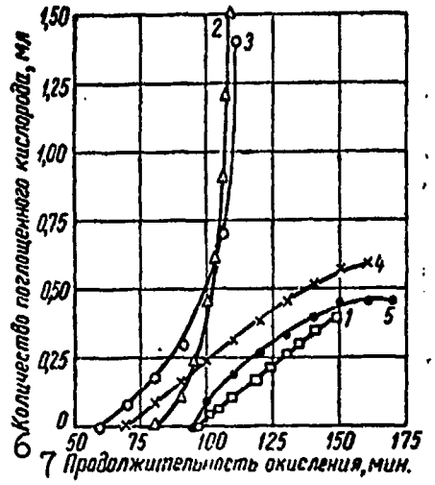
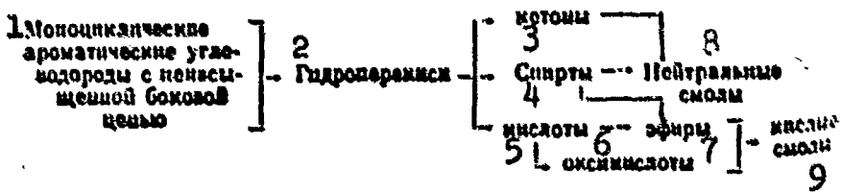



Fig. 216. Effect of VB-24 bronze on fuel oxidizability. 1) Initial fuel; 2) in presence of 5 $cm^2$ of freshly polished bronze; 3) the same, 10 $cm^2$; 4) in presence of 5 $cm^2$ oxidized bronze; 5) the same, doubly oxidized bronze; 6) quantity of oxygen absorbed, ml; 7) duration of oxidation, min.

On the basis of what we have said, the mechanism of self-oxidation of low stability hydrocarbons in VRD fuels during storage can be represented as follows:




1) Monocyclic aromatic hydrocarbons with unsaturated side chain; 2) hydroperoxides; 3) ketones; 4) alcohols; 5) acids; 6) hydroxy acids; 7) esters; 8) neutral gums; 9) acid gums.

Oxidation products present in the fuel have a great effect upon fuel stability under storage conditions. For T-1, TS-1, and T-2 fuels, removal of oxidation products leads to increased stability under sto-

age conditions while for fuels with cracked components, on the other hand, there is a sharp drop in stability [48]. The presence of oxidation products in fuels affects storage stability in different ways. Figure 214 graphically illustrates the effect of hydroxy acids and acid and neutral gums on the oxidizability of fuels with cracked components. When hydroxy acids and acid-type gums are added to a fuel, the fuel oxidizes rapidly with an increase in the existent gum and acidity. Neutral gums have no noticeable effect upon fuel acidity. Phenyl compounds have the same effect upon fuel acidity, as we can see from Fig. 215. Upon addition of phenyl compounds, the fuel oxidation curves by the PK method differ little from each other [47].

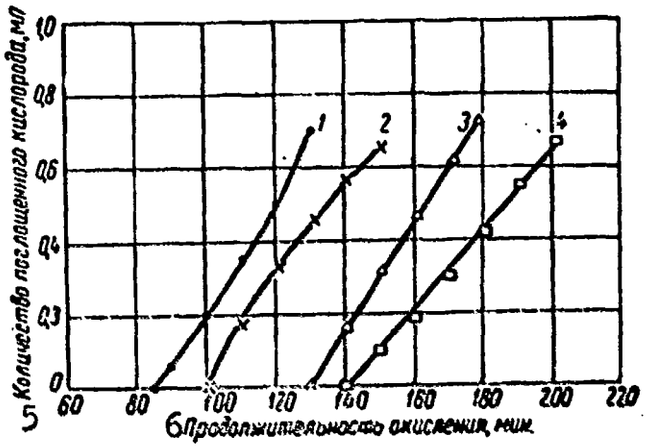



Fig. 217. Effect of elementary sulfur on fuel oxidizability. Concentration of elementary sulfur (%): 1) 0.001; 2) 0.003; 3) 0.005; 4) 0.008. 5) Amount of oxygen absorbed, ml; 6) duration of oxidation, min.

In addition to oxidation products, metals in contact with a fuel have a considerable effect upon fuel stability under storage conditions. Copper and its alloys, with which a fuel may come into contact while it is being used, have the greatest effect upon fuel stability. It is sufficient to state that the amount of copper may reach 20-25% in the ash residue for T-1 and TS-1 fuels.

In addition, certain fuels of the wide-boiling type such as the

American JP-3 and JP-4 fuels have the active sulfur compounds removed by copper salts. After such purification, copper salts remain in the fuel in negligible quantities (0.3-0.7 mg/liter); they sharply impair stability under storage conditions.

Figure 216 shows graphically the effect of VB-24 bronze on the oxidizability of a fuel according to the PK method [13]. It follows from the data given that VB-24 bronze sharply decreases the induction period of a fuel and increases the oxidation rate after the end of the induction period. It turns out, however, that only bronze with a clean surface has this effect. If an oxide film forms on the surface of the bronze, the catalytic activity of the bronze is almost eliminated. A clean copper surface has a similar effect.

In order to prevent catalytic action of metals on VRD fuels (JP-4, DERD-2486, Air 3407, and NATO-F-42) 5.6 mg/liter of the metal deactivator N,N'-disalicylidene-1,2-propane diamine is used abroad as an additive [49, 50, 51].

Sulfur compounds have a great effect upon the stability of VRD fuels obtained from sulfurous petroleums. The effect of elementary sulfur on fuel oxidizability in the presence of VB-24 bronze is shown in Fig. 217. As the elementary sulfur concentration rises, the induction period drops considerably. This results from the fact that elementary sulfur plays the role of an oxidation inhibitor, and also decreases the catalytic effect of the bronze, forming a low-activity sulfide film on its surface.

A study of the effect of other sulfur compounds on VRD fuel stability has shown that mercaptans, sulfides, thiophanes, and thiophenes decrease the fuel induction period [17].

Oxidation-inhibiting additives are used to obtain VRD fuels that are stable under storage conditions (see Chapter 14).

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## Chapter 22

## THERMAL STABILITY OF JET FUELS

The fuels used in large quantities for VRD are ligroin-kerosene fractions and, to some extent, gas-oil fractions obtained by direct distillation of petroleums. Fuels containing components obtained by secondary methods of petroleum refining have been tested as standby fuels. The [Soviet] T-4 fuel, for example, consists of direct-distillation and thermal-cracking components; the American JP-4 fuel may contain cracking products.

A new quality specification set forth for VRD fuels is high thermal stability, i.e., the ability to retain the necessary operational properties under elevated-temperature conditions. The appearance of this index in the specifications for VRD fuels stemmed from the creation of supersonic aircraft.

At flight speeds exceeding the speed of sound, aircraft are subjected to considerable aerodynamic heating. Calculations indicate that in flight at a speed M = 2 to 3* for several hours, the aircraft's skin temperature may reach and exceed 200-250° [1], an effect that causes heating of the fuel in the tanks. Moreover, the fuel is used as a coolant for the oil radiators and various other elements of the aircraft in most supersonic and subsonic models, and this gives rise to further heating of some of the fuel.

It has been found that under the influence of high temperatures (above 100°), deposits begin to form in the presence of oxygen in direct-distilled fuels that are regarded as chemically stable, follow-

ing fuel-filter elements and small clearances between rubbing pairs.

This interferes with the performance of the flow-regulating apparatus, reduces the fuel supply to the engine, and ultimately interferes with normal operation of the engine.

At the present time, the term "thermal stability" of fuels also implies their resistance to the formation of scale at elevated temperature.

## METHODS OF INVESTIGATING AND MONITORING THERMAL STABILITY OF FUELS

The laboratory methods that have recently been developed for evaluating the thermal stability of fuels may be subdivided into two basic groups: a) static and b) dynamic methods.

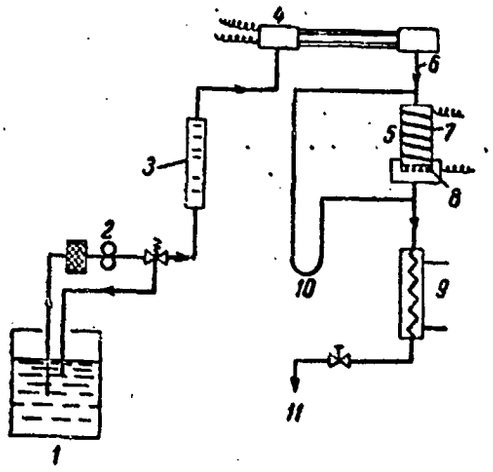



Fig. 218. Diagram of standard apparatus (CFR) for determining thermal stability of fuels [5]. 1) Fuel; 2) pump; 3) flowmeter; 4) preheater; 5) filter holder; 6) thermocouple for measurement of fuel temperature; 7) thermocouple for measurement of filter temperature; 8) filter; 9) radiator; 10) pressure gauge; 11) drainage.

In the static methods, a definite volume of fuel is oxidized at elevated temperature and its thermal stability evaluated by the quantity of scale formed.

In the dynamic methods, the fuel, which has been heated to a specified temperature, is continuously pumped through a filter and its thermal stability evaluated by the test time elapsing before the filter is completely clogged by the deposit.

Of the static methods, the bomb-oxidation method [3, 4, 6, 7] and the LSA-apparatus method [8, 9, 11, 32] have come into most widespread use. In bomb oxidation [7], 100 ml of the fuel in a glass beaker is placed in the steel bomb used for determining gasoline induction periods and oxidized at an air pressure

of 3 atmospheres for 4 hours at a temperature of 150°. In the LSA instrument (Chapter 3), 50 ml of fuel are oxidized in hermetically sealed glass flasks for 1 hour at a temperature of 150°; an electrolytic-copper plate serves as a catalyst (GOST 9146-59).

After oxidation in the bomb or in the LSA device, the fuel is filtered through a "white ribbon" paper filter and the quantity of deposit that has formed in it is determined.

The dynamic methods of evaluating the thermal stability of fuels have also been formulated in various versions [3, 4, 5, 10, 12]. In the USA, a dynamic method (CFR method) is standard. The thermal stability is determined in a CFR coker (Fig. 218), which was originally known as the "Erdco coker" [4, 12, 13].

In the CFR coker, the fuel is heated to a temperature of 150-230° in an electrically-heated aluminum tube and passed through a 20-μ-mesh filter made of fused stainless-steel powder. A paper filter element or an element of some other material may also be used in the CFR coker. The filter is provided with electric heating to permit further heating of the fuel to 205-260°. The fuel is fed at a constant rate of 2.7 kg/hour at an initial pressure of 10.5 atmospheres. The test time is 300 minutes; about 15 liters of fuel are required for the test. For experimental fuels, a variant of the method that uses circulation and requires only 600 ml of fuel is employed.

The thermal stability of the fuel is expressed in terms of the pressure drop across the filter after a 300-minute test (Table 170), or, if the filter is plugged earlier, the test time until the maximum attainable pressure-drop value (470 mm hg) is attained.

The other dynamic methods are similar to the CFR method; they differ as regards the physical design of the apparatus and the test technique.

In the [Soviet] LTS apparatus [10, 16] (Fig. 219), fuels are tested for thermal stability at several temperatures.

The data obtained on the LTS apparatus and the LSA instrument (Table 171) indicate that both the static and dynamic methods enable us to distinguish between fuels on the basis of their thermal stability, as well as to evaluate the influence of purification of the fuels and addition of additives.

The laboratory methods of determining the thermal stability of fuels enable us to form correct estimates of their behavior under real conditions. For example, a fuel having a CFR thermal stability of 25 minutes (a "25-minute fuel") caused clogging of the fuel system after 2-4 hours under analogous conditions in a real installation, while a "100-minute fuel" produced the same effect after 7-11 hours [29].

TABLE 170

Thermal-Stability Specifications for American Hydrocarbon Fuels [14]

| 1Показатели | 2Марка топлива | | |
|---|---|---|---|
| | JP-5 | JP-6 | 3перспективное топливо JP-X |
| 4Метод испытания | 5Однопроходной | 5Однопроходной | 6С циркуляцией |
| 7Температура испытания, °С* | 140/204 | 204/260 | 232/260 |
| 8Максимально допустимый перепад давления на фильтре за 300 мин., мм рт. ст. | 304 | 254 | 25 |

* The number before the slash indicates the fuel temperature in the preheater, while the following number indicates the fuel temperature at the filter.

1) Index; 2) fuel type; 3) JP-X prototype fuel; 4) test method; 5) single-pass; 6) with circulation; 7) test temperature, °C*; 8) maximum admissible pressure drop across filter after 300 minutes, mm Hg.

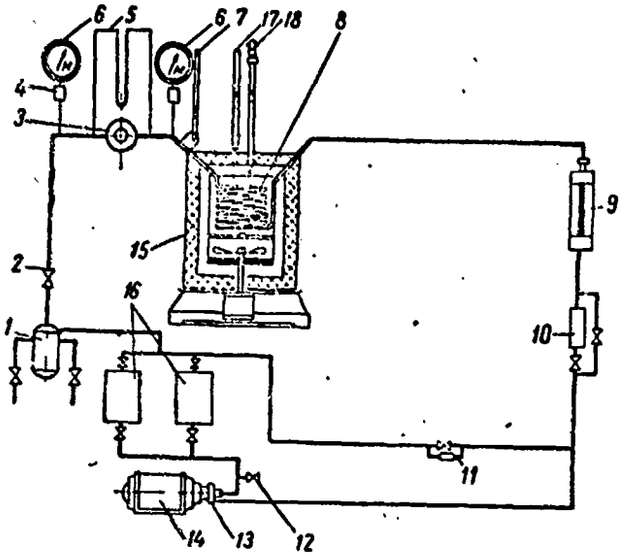



Fig. 219. Diagram of LTS apparatus for determining thermal stability of fuels under dynamic conditions [10]. 1) Radiator; 2) pressure valve; 3) filter in holder; 4) manometer damper; 5) differential mercury manometer; 6) spring manometer; 7) thermometer for measuring pure temperature; 8) heating coil; 9) rotameter; 10) first filter; 11) reduction valve; 12) release valve; 13) gear pump; 14) electric motor; 15) thermostating heater air jacket; 16) fuel tanks; 17) thermometer for measuring air temperature; 18) contact thermometer.

TABLE 171

Results of Determination of Fuel Thermal Stability in LSA and LST Apparatus [9] ($t = 150^{\circ}$)

| 1 Образцы топлив | 2 Количество осадка при окислении в приборе ЛСА, мг/100 мл | 3 Время забивки фильтра установки ЛТС, мин. |
|---|---|---|
| № 1 | 24,8 | 245 |
| № 2 | 18,8 | 230 |
| № 3 | 13,8 | 240 |
| № 4 | 42,2 | 130 |
| 4 № 4, очищенный адсорбентом | 8,8 | >300 |
| 5 № 4 + 0,05% присадки А | 7,4 | >300 |

1) Fuel specimen; 2) quantity of deposit on oxidation in LSA instrument, mg/100 ml; 3) time to plugging of LST filter, minutes; 4) No. 4, cleaned by adsorbent; 5) No. 4 + 0.05% of additive A.

On the basis of numerous tests, a thermal-stability index of 300 minutes has been established in the USA for fuels tested by the CFR method.

## INFLUENCE OF TEMPERATURE ON DEPOSIT FORMATION IN FUELS AND THEIR THERMAL STABILITY

At storage temperatures, deposits form in VRD fuels at a very low rate [15].* At temperatures above 100-110°, the rate of formation of the deposits in commercial fuels increases sharply; for deposits to begin to form in a fuel, it is only necessary that the fuel be held for a short time (a few minutes) at elevated temperature.

Investigations carried out by both static [7] and dynamic methods [3, 16] have shown that while scaling is aggravated by elevated temperature for some fuels, most commercial fuels have a most "dangerous" temperature zone at about 120-190°. Within this zone, the rate of deposit formation and the rate or filter clogging by the deposits are at their maximum (Figs. 220 and 221). At higher temperatures (200-220°), the fuels filter without clogging the filters just as they do at lower temperatures (below 100-110°). The temperature zones of sedimentation are different for different types of fuels (Table 172). T-1 fuel begins to clog the filter at a lower temperature, while T-5 fuel and most specimens of TS-1 fuel begin this at higher temperatures. The temperature of fastest sedimentation for T-1 fuel is below that for many specimens of TS-1 and T-5 fuels. The thermal stability of the high-sulfur TS-1 fuel is heavily dependent on its origin; many specimens of fresh (recently refined) fuel of this grade do not plug the filters with deposits at all.

Fuel T-2 – a direct-distilled fuel of expanded fractional composition that contains gasoline fractions – filters without clogging the filters in the temperature range from 150-200°. Cracking kerosene

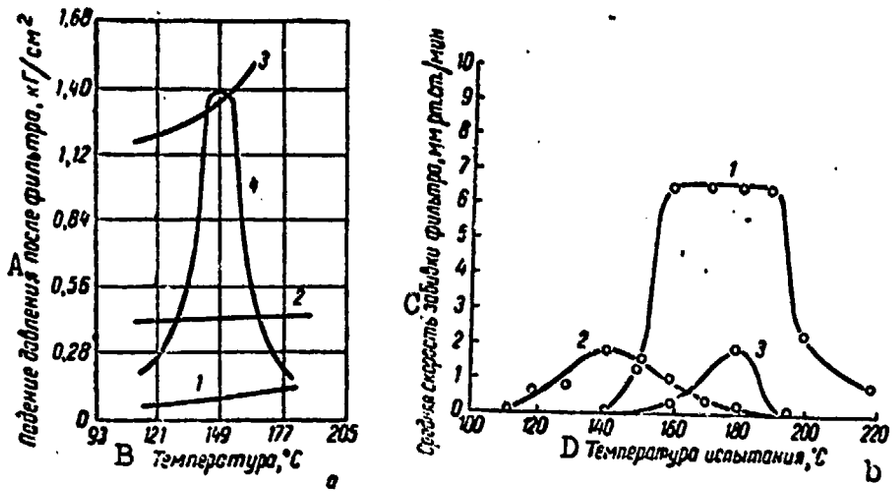



Fig. 220. Thermal stability of VRD fuels and its temperature dependence. a) Thermal stability of American VRD fuels as a function of temperature; test by dynamic method [3]; 1, 2, 3, 4) fuel specimens. b) Average rate of filter clogging as a function of temperature (test on LTS apparatus [16]); 1) Type T-5 fuel; 2) type T-1 fuel; 3) type TS-1 fuel. A) Pressure drop after filter, kgf/cm$^2$; B) temperature, °C; C) average rate of filter plugging, mm Hg/min; D) test temperature, °C.

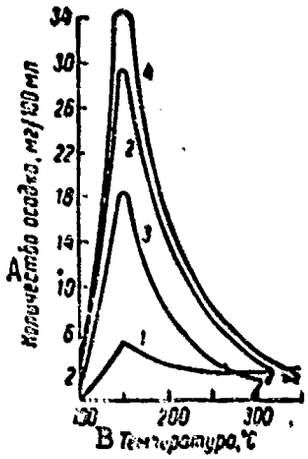



Fig. 221. Influence of temperature on deposit formation in TS-1 and T-1 fuels (bomb oxidation [7]). 1) TS-1; 2) T-1; 3) TS-1 with bronze; 4) T-1 with bronze. A) quantity of deposit, mg/100 ml; B) temperature, °C.

has lower thermal stability; its deposit-forming rate has reached its maximum at a temperature as low as 120°.

The initial temperature of formation of filter-blocking deposits sets a practical limit to the temperature range at which the fuel in question can be used. On heating, the properties of a fuel change as a result of oxidation of hydrocarbons, which results in increased acidity and increased tar content in the fuel. For commercial fuels produced by direct distillation, these changes are relatively minor on transient heating even to the highest test temperatures [16]. Apart from insoluble deposits, tarry de-

TABLE 172

Temperature Range of Sediment Formation in Jet Fuels (by dynamic method, LTS apparatus) [16]

| 1 Топливо | 2 Температура, °С: 3 начала забивания фильтра | 4 максимальной скорости забивания фильтра | 5 верхнего температурного предела забивания фильтра | 6 Термическая стабильность при температуре максимума забивания фильтра: 7 время до забивания фильтра, мин. | 8 средняя скорость забивания фильтра, мм рт. ст./мин |
|---|---|---|---|---|---|
| 9 Керосин прямой перегонки из сернистых нефтей (типа Т-1) | 110 | 140 | ~ 190 | 120—180 | 2,8—1,9 |
| 10 Облегченный керосин прямой перегонки из сернистых нефтей (типа ТС-1) | > 140—150 | 160—180 | ~ 190 | 120—300 | 2,8—1,1 |
| 11 Топливо на основе керосино-газойлевых фракций прямой перегонки (типа Т-5) | > 140 | 170—180 | > 200 | 50—120 | 6,9—2,8 |
| 12 Топливо на основе бензино-керосиновых фракций прямой перегонки (типа Т-2) | 13 В пределах температур 100—200° практически не образует осадков, забивающих фильтр | | | | |
| 14 Топливо на основе бензино-керосиновых фракций с продуктами крекинга (типа Т-4) | 16 120 и выше | 15 В зависимости от эффективности антиокислителя: 130—160 | — | 150—170 | 2,0—2,4 |
| 17 Керосин термического крекинга | > 100 | ~ 140 | > 160 | 50 | 6,9 |

1) Fuel; 2) temperature, °C; 3) onset of filter clogging; 4) maximum rate of filter clogging; 5) upper temperature limit of filter clogging; 6) thermal stability at temperature of maximal filter clogging; 7) time to clogging of filter, minutes; 8) average rate of filter clogging, mm Hg/min; 9) direct-distillation kerosene from low-sulfur petroleums (type T-1); 10) lightened kerosene from direct distillation of high-sulfur petroleums (type TS-1); 11) fuel based on kerosene-gas-oil fractions from direct distillation (type T-5); 12) fuel based on gasoline-kerosene fractions of direct distillation (type T-2); 13) within temperature range from 100 to 200°, practically no filter-clogging deposits form; 14) fuel based on gasoline-kerosene fractions with cracking products (type T-4); 15) depends on effectiveness of antioxidant; 16) 120 and higher; 17) thermal-cracking kerosene.

posits may form on hot metal surfaces of the fuel-system components (for example, in the oil radiator, etc.). The quantity of these deposits depends on the extent to which the fuel is oxidized and increases with increasing temperature and longer test times.

The influence of temperature on the formation of deposits in

fuels comes into evidence not only on heating, but also on cooling of the fuels from higher temperatures to temperatures from 150-130°. For certain fuels, extremely rapid deposit formation and filter blocking by these deposits is observed particularly during slow cooling of fuels that have been heated to a temperature of the order of 200° [3]. In this case, the same relationship prevails as in heating of fuels from the ambient temperature to higher temperatures (see Figs. 220 and 221) – the maximum rate of sediment formation corresponds to a certain temperature zone.

On the basis of their research, both foreign [3, 4] and Soviet [20] researchers have come to the conclusion that most ordinary commercial direct-distillation fuels have inadequate thermal stability. To raise the temperature at which the fuels can be used in engines, it will be necessary to improve the thermal stability of the fuels.

## COMPOSITION, STRUCTURE AND MECHANISM OF FORMATION OF DEPOSITS IN FUELS

The general qualitative laws governing sediment formation in fuels were set forth in Chapter 12. The present chapter will be concerned only with the data that are necessary for treating the problem of fuel thermal stability.

The deposits that form in the fuels at elevated temperatures are conglomerates of carboid particles cemented to one another by tarry substances. The tarry part of the deposit can be removed by processing with polar solvents.

In deposits obtained from fuels of the direct-distillation kerosene type, about 53-69% of tarry compounds and 47-31% of carboid compounds may be present [6]. The chemical nature of the deposits has not been ascertained with sufficient clarity; they are of oxidative origin, since they do not form in the absence of oxygen and contain

TABLE 173

Elementary Composition of Deposits and Their Ash Content as Functions of Conditions of Formation and Fuel Type [5, 6, 17]

| 1 Топливо | 2 Условия образования осадков | 3 Зольность осадка, % вес. | 4 Состав осадка по элементам, % вес. | | | | |
|---|---|---|---|---|---|---|---|
| | | | C | H | S | O | N |
| 5 Керосин прямой гонки, обр. 1 | 6 120°, окисление в присутствии бронзы . . . | 7,3 * | 33,7 | 5,4 | 6,0 | 46,6 | 1,0 |
| 7 То же, обр. 2 | 8 То же . . . . . | 7,0 * | 20,1 | 5,4 | 8,1 | 49,7 | 0,7 |
| 9 Крекинг-керосин | » . . . . . | 16,1 * | 49,6 | 5,4 | 8,1 | 18,5 | 2,3 |
| 10 Реактивное топливо США, обр. 1 | 11 204°, окисление без металла . . . . . | 7,0 | 67,0 | 6,0 | 4,0 | 13,5 ** | 2,5 |
| 12 США, обр. 2 | 13 В полноразмерной топливной системе . . | 13a В основном $Fe_2O_3$ | 50,0 | 4,7 | 6,0 | — | 2,3 |
| 14 Тип N | 15 150°, окисление в металлической аппаратуре . . . . . | 31,3 | 41,1 | 6,5 | 5,6 | 46,8 | — |
| 16 Керосино-газойлевые фракции | 17 То же . . . . . | 51,7 | 69,3 | 9,5 | 0,5 | 20,6 | — |

* The ash-forming element content (without oxygen) is given here.
** By subtraction.

1) Fuel; 2) conditions of deposit formation; 3) ash content of deposit, % by weight; 4) composition of deposit by elements, % by weight; 5) direct-distilled kerosene, specimen 1, 6) 120°, oxidation in presence of bronze; 7) same, specimen 2; 8) same; 9) cracking kerosene; 10) American jet fuel, specimen 1; 11) 204°, oxidation without metal; 12) USA specimen 2; 13) in full-scale fuel system; 13a) basically $Fe_2O_3$; 14) type N; 15) 150°, oxidation in metallic apparatus; 16) kerosene-gas-oil fraction; 17) same.

large quantities of that element (Table 173).

The tarry part of the deposits is characterized by high acidity (up to 230-290 mg of KOH per 1 g [6]), and, in cases where the deposits are obtained from a fuel containing a cracking component, by a high iodine number as well (about 90 g of iodine per 100 g [6]). When the deposits are examined by spectral methods, it is found that the carboxyl and aldehyde functional groups predominate in them. The presence of the aromatic ring has also been established in the deposits

by these same methods. Inorganic ash-forming elements may constitute a considerable part of the deposits. The ash content of the deposits depends on the conditions under which they formed and the chemical nature of the fuel. Table 173 presents data on the elementary composition and ash content of the gross deposits formed in fuels of different origins.

On oxidation of fuel, the deposits formed contain ash elements in quantities that produce up to 3-7% of ash, even in the absence of metallic surfaces. On single-pass pumping of fuel through a metallic heater, the quantity of ash in the deposit increases to 15-20%, while on multiple circulation of hot fuel in a metal apparatus, the deposit ash content reaches 30-50%. Deposits formed from fuels possessing high corrosive aggressiveness contain the largest amounts of ash.

Spectral analysis of the ash indicates that a wide variety of elements is present in it (see Chapter 22 [sic]).

Metals in contact with a fuel that oxidizes at elevated temperature may have an influence on the quantity of deposit formed in the fuel, not only as a result of corrosion processes, but also because they are oxidation catalysts.

Copper and copper alloys have the strongest effect in oxidizing fuels and forming deposits in them; steel and aluminum-alloy specimens have shown much lower catalytic activities. As the temperature rises from 120 to 200-250°, the differences between the catalytic activities of the metals tend to level off.

The dispersion of the deposits is an important factor in filtration of the fuels through fuel filters. The quantity of deposit sufficient to stop the filter completely under the conditions of constant fuel flow is very small and reckoned in milligrams per 1 $cm^2$ of filter surface. Depending on temperature and the properties of the

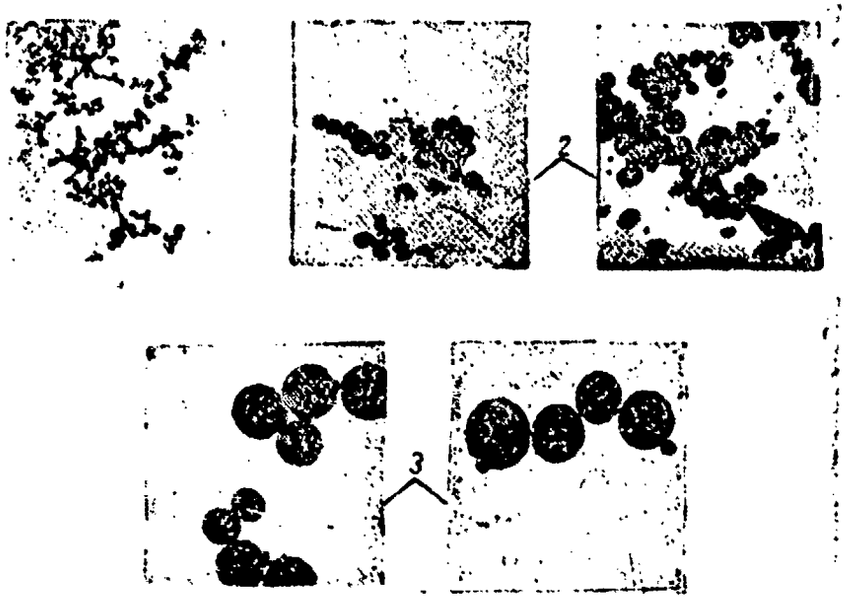


Fig. 222. Electron micrographs of high-temperature deposits and sediments (10,000 x). 1) Gross deposit from direct-distilled kerosene in metallic apparatus, 150°; 2) tarry part of deposit from fuel with cracking products, 200°, in glass apparatus; 3) carboid part of deposit from direct-distillation fuel, 200°, in glass apparatus.

fuel, the filter-blocking deposits are characterized by different dispersions and densities.

At the initial temperatures of deposit formation (120-140°, depending on fuel type), the filters are blocked by very fine particles of a light gray color that penetrate into their pores and are almost invisible on the surface. At higher temperatures (150-200°), the deposits become dark and pile up on the surface of the filter. It has been established that the particle size of the deposits that form in T-5, T-1 and TS-1 fuels does not exceed 50 μ at temperatures below 150°, while it runs to 50-120 μ at temperatures from 150-250° [18].*

The presence of particles of different shapes and sizes in the deposits was established by electron-microscope examination. Crystalline and amorphous (pastelike, granular) particles of oblong or spherical shape and ranging in size from tenths of a micron to several

microns were detected [3, 4].

Figure 222 shows electron micrographs of certain deposits, as well as the tarry sediment that formed on the metallic surfaces.* The insoluble part of the deposit consists of individual spherical particles about 0.5 μ and smaller in diameter and joined together in branched chains. These chains are also held together by tarry substances, with the result that conglomerates of particles form and block the fuel filters.

The above data on the composition and structure of the deposits justify the assumption that they are formed basically as a result of polymerization and condensation of the oxidation products of nonhydrocarbon compounds present in the fuels [4, 5]; an increase in temperature sharply accelerates the deposit-formation process. It is also assumed that the precipitation of deposits in a definite temperature zone is the result of a change in the state (coagulation) of the oxidation products of nonhydrocarbon impurities present in the fuel in the form of a colloidal solution [16].

INFLUENCE OF CHEMICAL COMPOSITION OF FUELS ON THEIR THERMAL STABILITY

In commercial hydrocarbon fuels of the aviation-kerosene type, there are present in insignificant quantities certain nonhydrocarbon compounds – sulfur, nitrogen and oxygen compounds; traces of compounds containing metals may also be present. Their quantity does not normally exceed 1-2% [19, 20]. In [Soviet] aviation kerosenes, the content of sulfur compounds may run to 0.4-1%, that of nitrogen compounds to 0.15-0.5% [21] and that of oxygen compounds to 0.15-0.2% [19]. When gas oil fractions are included in VRD fuels, the content of nonhydrocarbons increases.

The composition of the deposits that form in fuels on heating to high temperatures indicates that it is precisely these nonhydrocarbons

that are the primary sources of deposit formation, since sulfur, nitrogen and oxygen compounds are always present in them in higher concentrations than in the initial fuel [3, 6, 17].

TABLE 174

**Thermal Stability of Specimens of Various Commercial Fuels and Their Hydrocarbon Components [20]**

| 1 Топлива | Термическая стабильность при температуре максимума осадкообразования (2) | | Температура максимальной скорости осадкообразования для данного образца топлива, °С (5) |
|---|---|---|---|
| | 3 время до забивки фильтра, мин. | 4 средняя скорость забивки фильтра, мм рт. ст/мин | |
| 6 Керосин прямой перегонки из малосернистых нефтей | 170 | 2,0 | 140 |
| 7 Углеводородная часть того же топлива | > 300 | 0,1 | |
| 8 Облегченный керосин прямой перегонки из сернистых нефтей | 185 | 1,9 | 180 |
| 9 Углеводородная часть того же топлива | > 300 | 0,01 | |
| 10 Керосино-газойлевые фракции прямой перегонки из малосернистых нефтей | 45 | 6,6 | 160 |
| 11 Углеводородная часть того же топлива | > 300 | 0,3 | |
| 12 Керосин термического крекинга | 50 | 6,5 | 140 |
| 13 Углеводородная часть* того же топлива | > 150 | 1,2 | |

* The elimination of nonhydrocarbon compounds may not be complete.

1) Fuel; 2) thermal stability at temperature of maximum deposit formation; 3) time to blocking of filter, minutes; 4) average rate of filter blocking, mm Hg/min; 5) temperature of maximum deposit-formation rate for given fuel specimen, °C; 6) direct-distillation kerosene from low-sulfur petroleums; 7) hydrocarbon part of the same fuel; 8) lightened direct-distillation kerosene from high-sulfur petroleums; 9) hydrocarbon part of the same fuel; 10) kerosene-gas-oil fractions of direct distillation from low-sulfur petroleums; 11) hydrocarbon part of the same fuel; 12) thermal-cracking kerosene; 13) hydrocarbon part* of the same fuel.

When the nonhydrocarbons are eliminated from the fuel (for example, by adsorbent purification), its thermal stability increases sharply (Table 174) [20]. On the other hand, when nonhydrocarbons are added to a purified fuel, the thermal stability of the fuel de-

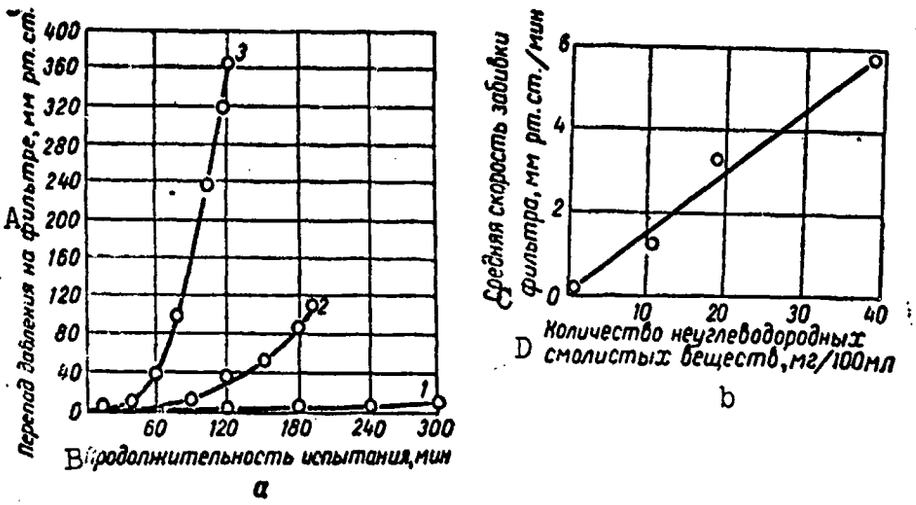



Fig. 223. Influence of nonhydrocarbon compounds in fuels on their thermal stability [20]. a) Thermal stability of type T-1 fuel with different amounts of nonhydrocarbon compounds: 1) Commercial fuel specimen; 2) 38 mg/100 ml of nonhydrocarbons added; 3) 150 mg/100 ml of nonhydrocarbons added. b) Average rate of filter blocking as a function of amount of nonhydrocarbons added. A) Pressure drop across filter, mm Hg; B) duration of tests, min; C) average rate of filter blocking, mm Hg/min; D) quantity of tarry nonhydrocarbons, mg/100 ml.

teriorates in proportion to the concentration of the impurities introduced (Fig. 223) [20].

The influence of specific nonhydrocarbon compounds on the thermal stability of fuels has not yet been studied. There are only occasional references to the effect that among the sulfur compounds present in the fuels, the polysulfides, higher aromatic mercaptans and aliphatic mercaptans have the strongest tendencies toward oxidative transformations. The other sulfur compounds are practically inert [3]. It is indicated that certain sulfur compounds in petroleum are thermally unstable even at temperatures as low as 130-150° [22, 23]. Among the nitrogen compounds, the least stable are pyrrole and the aliphatic triamines [3].

Apart from nonhydrocarbon impurities, the composition of the hydrocarbon part of a fuel may influence its thermal stability.

The thermal stabilities of the various groups of hydrocarbons have not yet been adequately studied. Certain authors are of the opinion that as regards thermal stability, the hydrocarbons array themselves in order of their tendency to liquid-phase oxidation [14]. This view is supported by data on the thermal stability of certain specific hydrocarbons [15] and a number of synthetic fuels [8, 25].

Among the hydrocarbons investigated, the bicyclic aromatic hydrocarbons have the poorest thermal stability (Fig. 224). Both saturated and unsaturated aliphatic hydrocarbons are highly stable.

Data on the very low thermal stability of polyalkylbenzene, which apparently contains bicyclic aromatic hydrocarbons, and the high [ thermal stability] of the synthol kerosene fraction, which consists of aliphatic hydrocarbons, are in good agreement with the above [8]. Naphthene-base fuels possess excellent thermal stability and fuels based on isoparaffins are rated very high in this respect [25].

The high stability of synthetic fuels as compared to commercial fuels may be accounted for not only by their hydrocarbon composition, but also by the absence of nonhydrocarbon impurities.

Olefin-aromatic hydrocarbons, the content of which in direct-distilled fuels may reach 2%, are regarded as a probable source of sediment formation [19].

On addition of cracking kerosene to direct-distilled kerosene, the thermal stability of the latter deteriorates sharply. However, the unsaturated kerosene hydrocarbons exert an influence considerably weaker than that of the nonhydrocarbons that accompany them (Fig. 225) [20].

Available experimental data permit us the conclusion that the thermal stability of the hydrocarbon part of commercial fuels is ade-

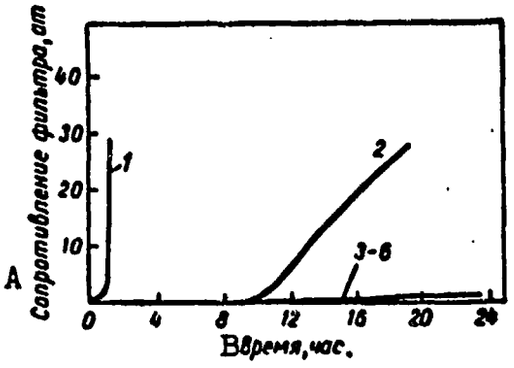



Fig. 224. Thermal stabilities of certain individual hydrocarbons [15] (test by dynamic method at a heater temperature of 232°, a filter temperature of 204°, and filter pores 5 μ in diameter). 1) α-methylnaphthalene; 2) tetralin; 3) cis-decalin; 4) dodecanes; 5) dodecene-1; 6) cetene. A) Resistance of filter, atmospheres; B) time, hours.

Fig. 225. Influence of cracking-kerosene admixture and hydrocarbon part thereof on thermal stability of direct-distilled fuel [20]. 1) With cracking kerosene; 2) with hydrocarbon part of cracking kerosene. A) Average rate of filter blocking, mm Hg/min; B) content of hydrocarbon part or cracking kerosene in mixture, % by volume.

quately high; the basic sources of deposit formation are the nonhydrocarbons present in the fuels. As a result, the thermal stability of the fuels is not an additive property; when fuels are mixed, the mixture has a thermal stability closer to that of the poorer fuel.

## METHODS OF IMPROVING THERMAL STABILITY OF FUELS AT ELEVATED TEMPERATURES

The formation of deposits in fuels at elevated temperatures may be reduced by two fundamentally different methods: a) by raising the thermal stability of the fuels; b) by changing the conditions under which the fuel is used – by excluding contact of the fuel with air.

The thermal stability of fuels is raised when they are purified of compounds that act as deposit-formation sources or when special additives are introduced.

### Influence of Various Purification Measures

In sulfuric-acid purification, a considerable part of the nonhydrocarbons is eliminated from fuels and the thermal stability of

TABLE 175

Thermal Stability of JP-X Fuels Produced by Hydrogenating Aromatic Concentrate, as a Function of Depth of Hydrogenation of Raw Material [14]

| A Показатели | B № образцов топлив | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| C Количество негидрогенизированных ароматических углеводородов, % объемн. | 1 | 12 | 17 | 21 |
| D Содержание серы в гидрогенизате, % вес. | 0,001 | 0,033 | 0,020 | 0,056 |
| E Термическая стабильность: | | | | |
| a а) время испытания, мин. | 300 | 300 | 300 | 125 |
| b б) температура испытания* | 232/260 | 232/260 | 232/260 | 232/260 |
| c в) перепад давления на фильтре, мм рт. ст. | 5 | 405 | 200 | 625 |

* The figure before the slash indicates the temperature of the fuel in the preheater, and the following figure the temperature of the fuel at the filter.

A) Index; B) fuel specimen No.; C) quantity of unhydrogenated aromatic hydrocarbons, % by volume; D) content of sulfur in hydrogenate, % by weight; E) thermal stability; Ea) test time, minutes; Eb) test temperature*; Ec) pressure drop across filter, mm Hg.

the fuel raised to the required level [13].

The Americans have tested a method in which the thermal stability of jet fuels is raised by purifying them with liquid sulfuric anhydride, but the prospects for this method are acknowledged to be poor [25]. Adsorbent purification of fuels gives good results [3, 20], but this method of purifying the fuels has not yet come into industrial use.

One of the promising processes for producing fuels with high thermal stability is hydraulic purification. In this process, the hydrocarbon part of the fuel is not subject to profound chemical modification, but sulfur, nitrogen and metals are removed, and we also observe saturation of olefins and decomposition of oxygen-containing compounds [26]. Use of this process makes it possible to obtain highly stable fuels from the Eastern high-sulfur petroleums of

the USSR [7].

Hydrogenation of aromatic concentrates separated by fractionation from products of catalytic cracking and reforming may be used to produce "exotic" fuels having high density and high heats of combustion and characterized by excellent thermal stability [14]. In the USA, these fuels are designated by the letters JP-X. However, the production of highly stable fuels requires total saturation of the aromatic concentrates by hydrogen and complete desulfurization (Table 175).

Fuels containing metallic hydrides (for example, boranes) and suspensions of metals (for example, lithium) in the fuels and hydrazine are also promising. The thermal stability of such fuels is given a lower point rating than that of hydrocarbon fuels [6].

In the USA, considerable attention is being devoted to the hydrocracking process [4, 25], since this method may be applied to residual fuels to produce types JP-4 and JP-5 VRD fuels whose thermal stability surpasses that of direct-distillation fuel [25]. However, the industrial acceptance of the hydrocracking process in the USA is not expected in the immediate future, since the residual fuels that form the raw material for it are widely used as boiler fuels [27].

Influence of Additives

The antioxidants used to raise the stability of fuels under the conditions of storage (Fig. 226) do not prevent the formation of deposits in the fuels at high temperatures [3, 4, 6]. The quantity of deposits formed in the fuels on heating may be reduced by the introduction of anticorrosion additives; in this case, the inorganic component of the deposit is reduced as a result of the reduced corrosive action of the fuel on the metals of the fuel-handling apparatus.

The use of additives that prevent growth of the deposit particles or break up particle lumps that have already formed (see Figs.

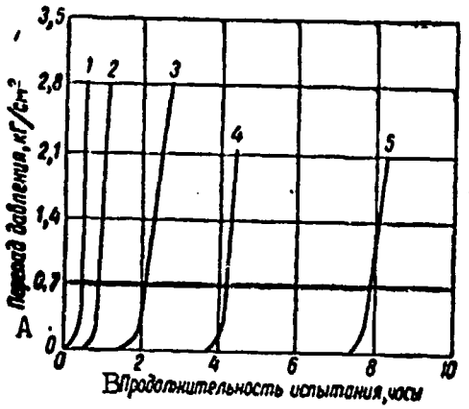
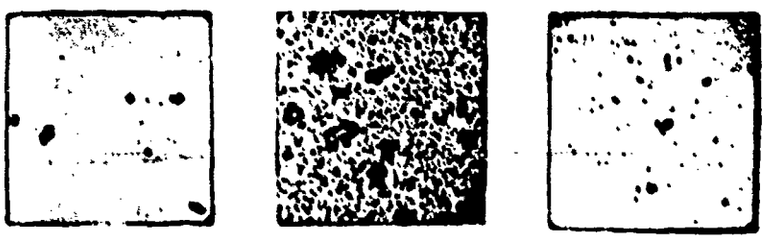



Fig. 226. Effect of antioxidants and dispersing additives in improving thermal stability of fuel [28]. 1) Fuel without additive; 2) with superior antioxidant; 3, 4, 5) with various dispersing additives. A) Pressure drop, kgf/cm$^2$; B) test time, hours.

226 and 227) is highly effective [28]. Nonmineral additives of the polar-polymer type [29, 30], which are products of copolymerization of compounds containing nitrogen bases with a component that improves their solubility in fuel (see Chapter 14), are the most effective. It has been proposed [29, 30] that detergent-type additives have a peptizing effect on colloidal oxidation-product particles and prevent their coagulation by holding the deposit in the form of a fine suspension.

Those additives that perform several functions, acting simultaneously as antioxidants, anticorrosion agents and detergents, are the best ones for raising the thermal stability of fuels. An additive



a b c

Fig. 227. Action of detergents on high-temperature deposits [29] (electron micrographs, 4100x). a) Initial fuel; b) same fuel after test by CFR method; c) fuel with detergent after CFR test.

designed to improve the thermal stability of fuels may also be formed by combining 2-3 additives possessing one or two of the functions enumerated above [30]. The maximum increase in fuel thermal stability may be achieved by combining purification with addition of "optimal" additives.

Effect of Filling Fuel-Tank Airspace with Inert Gas

If the fuel tanks are airtight, the airspace in them may be filled with either air or an inert gas, supplied under a certain pressure, as the fuel is consumed. Formation of deposits falls off sharply in fuels that are under pressure exerted by an inert gas (Table 176).

To gain anything, the air must be eliminated thoroughly from the fuel tanks, since even a minor admixture of oxygen to the inert gas will contribute to increased deposit formation (Fig. 228). Similar results were obtained in tests of TS-1 fuel at temperatures from 100 to 200° by the dynamic method [31]; it was established that in the presence of a pillow of nitrogen or of the fuel's own vapor in the space above it, the thermal stability of the fuel increased considerably. Under the test conditions, a 3.5-4.2-% oxygen content in the nitrogen did not have such a sharply detrimental effect as in static tests run on T-5 fuel.

TABLE 176

Influence of Nitrogen on Thermal Stability of T-5 Fuel [8] (oxidation in LSA apparatus, t = 200°)

| 1 Время окисления | 5 Количество осадка, мг/100 мл | |
|---|---|---|
| | в атмосфере 6 воздуха | в атмосфере 7 азота |
| 2 10 мин. . . . . | 16.8 | 8 Нет |
| 3 6 час. . . . . | 10.2 | 1.2 |
| 4 8 » . . . . . | 10.2 | 1.1 |

1) Oxidation time; 2) 10 minutes; 3) 6 hours; 4) 8 hours; 5) quantity of deposit, mg/100 ml; 6) in air atmosphere; 7) in nitrogen atmosphere; 8) none.

A certain amount of attention has been devoted to this method of countering accumulation of deposits in engine fuel systems in the USA [4].

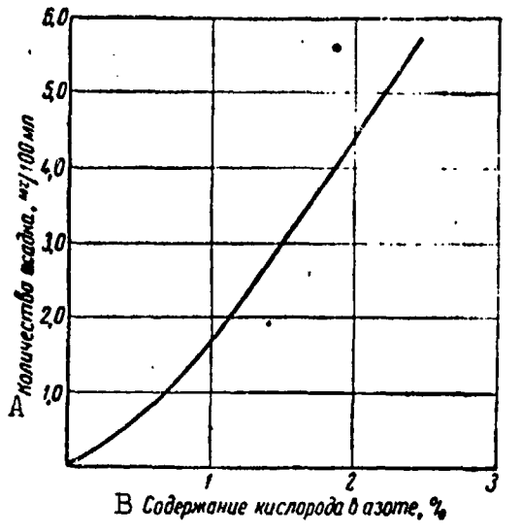



Fig. 228. Influence of oxygen content in nitrogen on formation of deposits in fuel at 200° (oxidation in LSA apparatus, 6 hours). A) Quantity of deposit, mg/100 ml; B) content of oxygen in nitrogen, %.

## CHANGE IN THERMAL STABILITY OF FUELS DURING STORAGE

Commercial VRD fuels produced by direct distillation of petroleum can be stored for long periods (several years) without undergoing any noticeable changes in their physicochemical properties. Observations of the thermal-stability changes undergone by fuels during storage were begun only during the last few years.

The changes to which the nonhydrocarbon components of fuels are subject during storage have not been given adequate study. The data available on this problem (see Chapter 10) lead us to the conclusion that nitrogen and sulfur compounds in the fuels form insoluble deposits even under normal storage temperatures, but that this process unfolds at a negligible rate. In experimental storage of jet fuels under various climatic conditions in the USA (24 fuel specimens were placed in the experimental storage), insoluble deposits formed in quantities that varied as a function of the conditions and time of storage [15]. In fuels containing a catalytic-cracking component, as much as 30 mg of insoluble products per 100 ml were found after 2-3 years of storage in a torrid climatic zone. The filterability of all fuels, including direct-distilled fuels (Fig. 229) [15] deteriorated during storage under normal temperature conditions. The insoluble deposits form in greater quantities in storage of higher-molecular-weight (diesel) fuels.

In [Soviet] VRD fuels, insoluble deposits formed in small quanti-

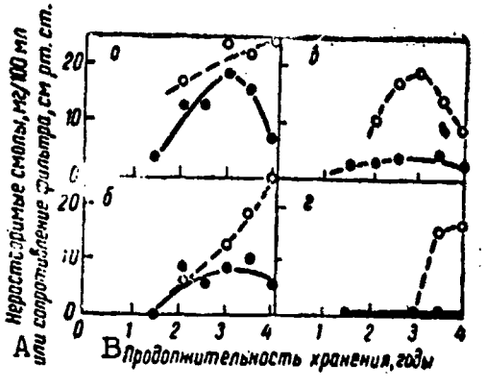



Fig. 229. Influence of storage on formation of insoluble deposits and filterability of jet fuels [15] (storage in torrid zone, filterability at normal temperature). a) Thermal-cracking fuel; b) mixture of direct-distillation and catalytic-cracking fuels; c) mixture of direct-distillation, catalytic-cracking and thermal-cracking fuels; d) direct-distilled fuel. A) Insoluble tars, mg/100 ml or filter resistance, cm Hg; B) storage time, years.

ties during artificial aging (at 50°) of fuels under laboratory conditions (2-4 mg/100 ml over 7 months of laboratory storage).

The formation and growth of insoluble particles in direct-distilled fuels during storage were recorded with the aid of an electron microscope (Fig. 230). As will be seen from the micrographs, changes in fuel specimens that had had a year of storage resulted in a considerable increase in the number of microscopically visible solid particles; their size had increased by several thousand percent. The accumulation and growth of solid particles in fuels during storage may result in deterioration of their thermal stability. It was noted that fuels that have been stored for long periods had thermal stabilities lower than those of fresh fuels [4].

Observation of the behavior of two different fuel specimens from direct distillation showed that the deterioration of thermal stability in storage is evidenced primarily in a drop in the initial temperature of deposit formation (Table 177).

The thermal stability of the fuels was monitored by the dynamic method using a pumping apparatus. In Specimen No. 1, the deposits formed in the temperature zone from 150 to 180° in a test run prior to storage; when the fuel was tested after a year of storage, the filter was blocked by the deposit rather rapidly even at 130°. In

Specimen No. 2, no deposit blocking of the filter was noted at temperatures of 140-180° prior to storage; after a year, the filter plugged up at 120°.

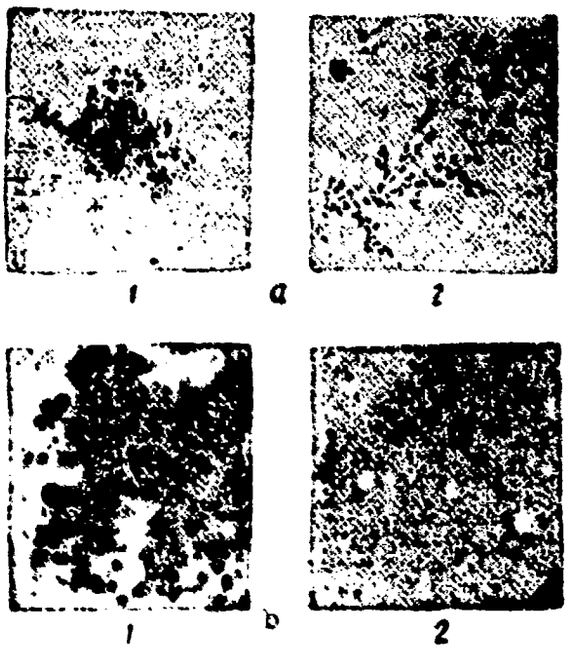



Fig. 230. Electron micrographs of fuels before and after one year of storage (magnification 1000 x). a) Fuel specimen before storage; b) fuel specimen after 1 year of storage. 1) TS-1; 2) T-5.

TABLE 177

Change in Thermal Stability of Direct-Distillation Fuels During Storage

| 1 | Образец № 1 | | Образец № 2 | |
|---|---|---|---|---|
| Продолжительность хранения | температура начала забивки фильтра, °С | средняя скорость забивки фильтра при 180°, мм рт. ст./мин. | температура начала забивки фильтра, °С | средняя скорость забивки при 160°, мм рт. ст./мин |
| 6 До хранения | <150 | 2.1 | >160 | 0.2 |
| 7 После 1 года хранения | <130 | 3.8 | <140 | 1.8 |

1) Duration of storage; 2) Specimen No. 1; 3) temperature of onset of filter blocking, °C; 4) average rate of filter blocking at 180° (160°), mm Hg/min; 5) Specimen No. 2; 6) before storage; 7) after 1 year of storage.

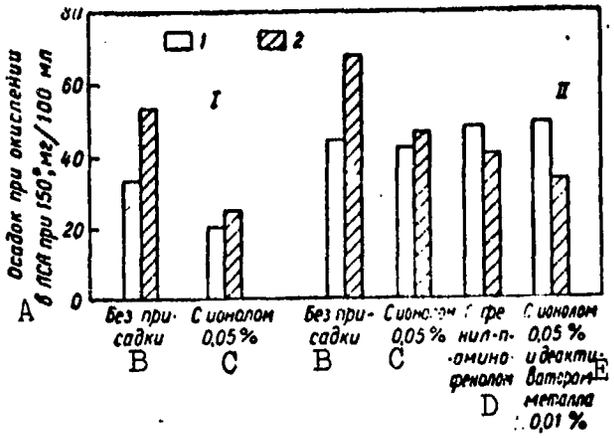



Fig. 231. Change in thermal stability of fuels during laboratory aging for 4 months at 50°C. I) T-1 fuel; II) T-5 fuel. 1) Before aging; 2) after aging. A) Deposit on oxidation in LSA at 150°, mg/100 ml; B) without additive; C) with 0.05% ionene; D) with phenyl-p-aminophenol; E) with 0.05% ionene and 0.01% metal deactivator.

The rate of filter blocking by the deposit at a given temperature increased after the fuel had been stored (see Table 177). Consequently, the admissible temperature limit at which the fuels can be used after storage drops markedly. It is therefore necessary to monitor carefully the changes in the thermal stability of fuels during storage.

On addition of certain additives to the fuel (antioxidants, metals deactivators), the changes in the fuel that result in deterioration of thermal stability are inhibited. For example, Fig. 231 shows the influence of these additives during laboratory storage of a fuel. Addition of the additives or a mixture of additives made it possible to maintain the initial thermal stability value in the fuel, while the thermal stability of a fuel stored under the same conditions without the additive deteriorated. A positive result was also obtained in storage of a fuel that had first been purified of nonhydrocarbon compounds, particularly if a stabilizing additive had

been introduced into the purified fuel.

It has been ascertained on examination of thermal-stability data on VRD fuels that although ordinary commercial fuels are unstable at temperatures typical for the conditions of supersonic flight, the problem of raising their thermal stability can be solved by accessible technological measures.

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[Footnotes]

738 The Mach number ("M") is the ratio of the aircraft's flight speed to that of sound, which is approximately 1194.5 km/hr [2] at $0^{\circ}$ and atmospheric pressure.

743 See Chapter 11.

749 The particle size was determined after the fuel had cooled to room temperature.

750 The electron micrographs were made by A.Ye. Sazonov.

[Transliterated Symbol]

738 ВРД = VRD = vozdushno-reaktivnyy dvigatel' = air-breathing reaction-thrust engine(s).

## Chapter 23

## PROMISING FUELS FOR AIR-REACTION ENGINES (VRD)

The effort to increase the flight speed, range, and altitude of aircraft with air-reaction engines has made extremely urgent not only those tasks associated with the improvement of the aerodynamic characteristics, materials, and design of jet aircraft, but it has also increased the importance of those less important jobs involving the production of higher-quality fuels. The primary trends in the improvement of fuels for air-reaction engines (VRD) involve increasing their power characteristics [1]. By power (energy) characteristics of fuels for VRD we mean the heat of combustion, density, and completeness of combustion. These characteristics play a decisive role in the efficiency of VRD and in the flight-technical characteristics of jet aircraft.

Thus the flight velocity of an aircraft with an air-reaction engine (VRD) at the present time is increased by using powerful thrust-augmented engines whose shortcoming lies in the fact that it involves an increased hourly fuel flow rate attaining 9000-18,000 kg/hr [2], which in turn results in a reduction in the flight range of the aircraft. In order to increase the flight range, the aircraft must carry, on board, a substantial reserve of thermal energy and this can be achieved by increasing the quantity of fuel and its heat of combustion. However, the future supersonic aircraft with air-reaction engines (VRD) have small fuselages and thin wings – and this restricts the possibility of loading large volumes of fuel aboard such aircraft.

Therefore the promising future fuels for VRD must have a higher specific weight which will provide for greater capacity, by weight, of the fuel tanks.

Another characteristic feature of the VRD aircraft of the future is the substantial flight altitude, reaching as high as 15,000-25,000 m. At these altitudes the combustion chambers of engines receive air in which the concentration of oxygen is reduced as a result of the over-all reduction of the mass concentration of oxygen in the ambient atmosphere at great altitudes. For example, the mass concentration of oxygen at an altitude of 15,000 m is 46 $g/m^3$, at an altitude of 25,000 m the concentration is 6.5 $g/m^3$, while at the surface of the earth the mass concentration of oxygen in the air reaches 288 $g/m^3$. Therefore under high-altitude conditions there is a substantial reduction in the completeness of fuel combustion as a result of which the flight range of aircraft is reduced.

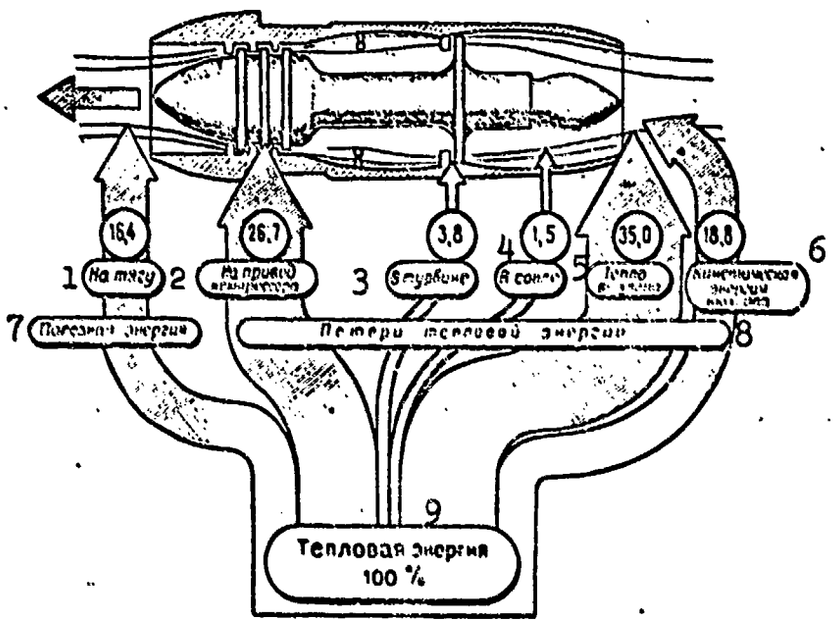


Fig. 232. The thermal balance of a TRD (turbojet engine). 1) On thrust; 2) to drive the compressor; 3) in the turbine; 4) in the nozzle; 5) heat of exhaust; 6) kinetic exhaust energy; 7) useful energy; 8) thermal-energy losses; 9) thermal energy, 100%.

In estimating the reserve of thermal energy aboard a jet aircraft, it should be borne in mind that only 16.4% of the thermal energy in a turbojet engine (TRD) is used to provide reaction thrust (Fig. 232). This also produces an increase in the fuel reserves aboard the jet aircraft, an increase which is required to provide for the thrust which would correspond to supersonic flight.

Recently, abroad, the volumetric heat of combustion, i.e., the heat of combustion referred not to a unit of weight but to a unit of fuel volume has, in addition to the mass heat of combustion, gained widespread acceptance in the evaluation (estimation) of the energy (power) characteristics of fuels. Anderton [3] proposed the utilization of an energy factor (calculated in accordance with the following formula) for a comparative evaluation of the energy characteristics of jet fuels:

$$a = 100 \frac{Q_v}{Q_v^e} \frac{Q_{ob}}{Q_{ob}^e} \%,$$

where $Q_v$ and $Q_{ob}$ are the mass and volumetric heats of fuel combustion; $Q_v^e$ and $Q_{ob}^e$ are the same quantities for the reference fuel.

To calculate the energy factor for some fuel with respect to T-1 fuel, the formula can be presented in the following form:

$$a = 116 \cdot 10^{-6} Q_v^2 \rho,$$

where $\rho$ is the density of the fuel at 20°.

A comparison of the energy characteristics of fuels for air-reaction engines (VRD) in accordance with the above-indicated energy factor will be valid only under ground conditions. In high-altitude flights the effect of completeness of combustion on the energy potentials of a fuel must be taken into consideration. The magnitude of completeness of combustion is, to a large extent, a function of the chemical composition of the fuel. Tests of fuels for VRD, carried out

by Scott, Stansfield, and Tait [4], have shown that as the flight altitude is increased the completeness of combustion of aromatic fuels is reduced somewhat more than in the case of paraffinic-naphthenic fuels. For example, at an altitude of about 11 km the completeness of combustion for fuels of a paraffinic-naphthenic base remains virtually the same as for a commercial fuel, whereas the completeness of combustion for aromatic fuels is reduced by 2% in comparison with a commercial fuel. Therefore a comparison of fuels in terms of energy factors must be carried out so as to take into consideration the effect of completeness of combustion. For example, for monocyclic aromatic hydrocarbons of the 300-350° fraction, the energy factor under ground conditions will be equal to 106%, whereas at an altitude of 11 km it will be equal only to 104%.

The energy factor may be used for a comparative evaluation of possible changes in aircraft flight range on a given fuel, as opposed to the flight range possible with T-1 fuel. A comparison of the results in the change of flight range according to the magnitudes of the energy factors and according to the data obtained by the well-known Breget [5] formula for the calculation of flight range of a "conventional" aircraft for which the weight of the fuel amounts to 65% of the total payload, shows discrepancies not exceeding 1.0-1.5%.

FUTURE PROSPECTS FOR THE UTILIZATION OF PETROLEUM FUELS FOR AIR-REACTION ENGINES [VRD]

An evaluation of the prospects of petroleum fuels for air-reaction engines (VRD) can be undertaken on the basis of a comparison of the energy (power) characteristics of these fuels. In terms of mass heat of combustion, the petroleum fuels T-1, TS-1, T-2, and T-5 show little difference between one another. The maximum heat of combustion is exhibited by the T-2 fuel (10,350-10,450 kcal/kg), and the minimum

heat of combustion is exhibited by the T-5 fuel (10,240-10,260 $\frac{kcal}{kg}$). The T-5 fuel has a density of 0.843-0.848; the T-2 fuel has a density of 0.760-0.770. The TS-1 and T-1 fuels occupy an intermediate position on the basis of these indicators. A calculation of the energy factors for commercial fuels yields the following data: T-2, 97%; TS-1, 98%; and T-5, 103%. This means that the fuels T-2 and TS-1 are inferior to the T-1 fuel in terms of energy characteristics by a factor of about 2-3%, whereas the T-5 fuel is better than the T-1 fuel by 3%. This in turn has its effect on an aircraft's flight range when these fuels are used.

Fuels of one and the same type, but derived from various petroleums, in terms of mass heat of combustion and density exhibit no significant difference. For example, the mass heat of combustion of the T-2 fuel derived from Tatar petroleums is equal to 10,440 kcal/kg; when this fuel is derived from Sakhalin petroleums, the mass heat of combustion is 10,340 kcal/kg; from Bashkiriya petroleums, 10,410 $\frac{kcal}{kg}$; and from Groznyy petroleums, 10,470 kcal/kg. Consequently, in deriving fuels for air-reaction engines (VRD) from petroleum crudes by means of conventional petroleum-refining methods we cannot count on any substantial improvement in the energy characteristics of the fuels.

The energy (power) characteristics of fuels for air-reaction engines (VRD) are, in great measure, dependent on the chemical and fractional composition of the fuels. The mean indicators of chemical and fractional composition of type T fuels indicate that the fuels T-1, TS-1, and T-2 exhibit varying chemical and fractional compositions. However, as has already been pointed out above, these differences are of no great significance with respect to the energy (power) characteristics of the fuels.

The energy characteristics of the hydrocarbons in the composition

TABLE 178

Energy (Power) Characteristics of Fuels for Air-Reaction Engines (VRD)

| 1 Пределы выкипания фракций, °С | 2 Углеводороды | 3 Теплота сгорания, ккал/кг | 4 Плотность $\rho_4^{20}$ | 5 Энергетический коэффициент, % |
|---|---|---|---|---|
| Т-1 | | | | |
| 125—150 | I | 10 420 | 0,7634 | 96 |
| | II | 9 880 | 0,8315 | 92 |
| 150—200 | I | 10 420 | 0,7926 | 100 |
| | II | 9 950 | 0,8313 | 95 |
| 200—250 | I | 10 400 | 0,8014 | 101 |
| | II | 9 890 | 0,9045 | 100 |
| 250—275 | I | 10 350 | 0,8283 | 103 |
| | II | 9 960 | 0,9092 | 102 |
| | III | 9 660 | 0,9653 | 100 |
| Т-2 | | | | |
| 100—150 | I | 10 480 | 0,7312 | 93 |
| | II | 9 960 | 0,8522 | 95 |
| 150—200 | I | 10 420 | 0,7662 | 97 |
| | II | 9 900 | 0,8744 | 97 |
| 200—250 | I | 10 350 | 0,7963 | 99 |
| | II | 9 960 | 0,8649 | 97 |
| ТС-1 | | | | |
| 100—150 | I | 10 540 | 0,7362 | 95 |
| | II | 9 870 | 0,8399 | 93 |
| 150—200 | I | 10 500 | 0,7514 | 96 |
| | II | 9 990 | 0,8385 | 94 |
| 200—250 | I | 10 510 | 0,7611 | 98 |
| | II | 9 890 | 0,8773 | 98 |

Note. Hydrocarbons: I – paraffinic-naphthenic; II – monocyclic aromatic; and III – bicyclic aromatic.

1) Limits of boiling for fractions, °C; 2) hydrocarbons; 3) heat of combustion, kcal/kg; 4) density, $\rho_4^{20}$; 5) energy (power) factor, %.

of a VRD fuel are of particularly great interest, depending on their distillation limits and chemical structure. Table 178 shows the energy (power) factors for a flight altitude equal to 11 km and for a group of hydrocarbons in the composition of the fuels T-2, TS-1, and TS-1 [sic – in accordance with Table 178 the proper order should probably read T-1, T-2, and TS-1], these hydrocarbons having various boiling limits. We can see from the data cited that for all fuels the paraffinic-naphthenic hydrocarbons exhibit higher energy factors than the mono- and bicyclic aromatic hydrocarbons. However, in this case as well, there is no substantial improvement in the energy characterist-

ics. For example, only the paraffinic-naphthenic hydrocarbons of the 250-275° fraction of the T-1 fuel have an energy factor equal to 103%. Other hydrocarbons of the T-1 fuel, as well as of the T-2 and TS-1 fuel, have energy characteristics below this magnitude.

A general rule is that the energy factors of hydrocarbons increase as the boiling point of these hydrocarbons rises. For example, the energy factors of the hydrocarbons of the 300-350° fraction of heavy Baku kerosene attain the following magnitudes (in %):

| | |
|---|---|
| Paraffinic-naphthenic | 105 |
| Monocyclic aromatic | 104 |
| Bicyclic aromatic | 103 |
| Tricyclic aromatic | 104 |

Consequently, the most promising fuels with increased energy characteristics are the paraffinic-naphthenic hydrocarbons boiling over at 300-350° and higher. The truth of the matter is that the aromatic hydrocarbons of this fraction also exhibit high energy factors; however, the utilization of these fuels in air-reaction engines (VRD) is associated with a number of operational difficulties (great tendency to scale formation, high temperature of crystallization, etc.). Given a positive solution to these difficulties, perhaps the entire fraction can be used without having to separate it into groups of hydrocarbons. Of the VRD petroleum fuels, the most promising are those distilled within a range of 300-350° and higher. Work is being done in this direction abroad; the intentions are to use light mazouts as VRD fuels [6].

The energy characteristics of hydrocarbon fuels for VRD can be increased by means of radioactive irradiation. With radioactive irradiation, the molecular weight of a fuel is increased. This results in a change in other fuel characteristics as well. For example, when the

American jet fuel JP-5 is subjected to an irradiation dosage of $5 \cdot 10^9$ r the viscosity of this fuel, at 38°, increases from 2 to 500 centistokes, the 50% boil-off point rises from 218 to 330°, and density increases from 0.84 to 0.94 [7].

Radioactive irradiation of jet fuels also has an effect on the thermal stability of these fuels. The thermal stability of fuels is improved by irradiation dosages of $5 \cdot 10^8 - 5 \cdot 10^9$ r and is impaired with a reduction in the irradiation dosage to $10^4 - 5 \cdot 10^8$ r.

SYNTHETIC HYDROCARBON VRD FUELS

If as a result of using high-boiling petroleum fractions the energy characteristics of VRD fuels can in the near future be increased by 4-5%, fuels with even higher energy characteristics can be obtained

TABLE 179

Energy Characteristics of Individual Hydrocarbons

| 1 Углеводороды | Теплотворная способность, ккал/кг | Плотность $\rho_4^{20}$ | Энергетический коэффициент, % |
|---|---|---|---|
| 5 *Парафиновые* | | | |
| 6 2,2-диметилпентан | 10 620 | 0.7739 | 101 |
| 7 3,12-диэтилтетрадекан | 10 530 | 0.7934 | 102 |
| 8 4,8,12-триметилгексадекан | 10 470 | 0.8027 | 102 |
| 9 2, 6, 10, 15, 19, 23-гексаметилтетракозан | 10 420 | 0.8003 | 102 |
| 10 *Нафтеновые* | | | |
| 11 1,1-дициклогексилэтан | 10 260 | 0.8931 | 109 |
| 12 2-изопропилдициклогексил | 10 390 | 0.9036 | 113 |
| 13 2,2-дициклогексилбутан | 10 310 | 0.9133 | 112 |
| 14 *Ароматические* | | | |
| 15 α-метилнафталин | 9 750 | 1.0030 | 108 |
| 16 2-метилдифенил | 9 525 | 1.0110 | 101 |
| 17 3-этилдифенил | 9 610 | 0.9993 | 104 |

1) Hydrocarbons; 2) heating value, kcal/kg; 3) density, $\rho_4^{20}$; 4) energy factor, %; 5) paraffinic; 6) 2,2-dimethylpentane; 7) 3,12-diethyltetradecane; 8) 4,8,12-trimethylhexadecane; 9) 2,6,10, 15,19,23-hexamethyltetracosane; 10) naphthenic; 11) 1,1-dicyclohexylethane; 12) 2-isopropyldicyclohexyl; 13) 2,2-dicyclohexylbutane; 14) aromatic; 15) α-methylnaphthalene kerosene; 16) 2-methyldiphenyl; 17) 3-ethyldiphenyl.

TABLE 180

Characteristic of High-Energy Fuels Based on Bi- and Polycyclic Naphthenes

| 1 Показатели | 2 Из нафтеновых фракций | | 3 Из ароматических углеводородов газойля каталитического крекинга | | | |
|---|---|---|---|---|---|---|
| | 4 Образцы | | | | | |
| | 1 | 2 | 1 | 2 | 3 | 4 |
| 5 Теплота сгорания: | | | | | | |
| 6 ккал/кг | 10 250 | 10 255 | 10 260 | 10 280 | 10 180 | 10 070 |
| 7 ккал/л | 8 880 | 8 990 | 8 950 | 9 020 | 9 560 | 9 860 |
| 8 Плотность $\rho_4^{20}$ | 0,863 | 0,874 | 0,872 | 0,876 | 0,936 | 0,976 |
| 9 Энергетический коэффициент, % | 105 | 106,5 | 106,5 | 107 | 112,5 | 115 |
| 10 Температура кристаллизации, °С | —60 | —60 | —60 | —42 | —40 | —40 |
| 11 Вязкость кинематическая при —18°, сст | 10,1 | 27,6 | 11,4 | 89 | 30 | 1800 |
| 12 Фракционный состав: | | | | | | |
| 13 10% выкипает, °С | 209 | 239 | 224 | — | — | — |
| 50% » » | 233 | 259 | 233 | 288 | 271 | 298 |
| 90% » » | 264 | 283 | 253 | — | — | — |
| 14 Термостабильность (перепад на фильтре), мм рт. ст. | 1 | Отсутствует | — | 2,5 | 4 | — |

1) Indicators; 2) from naphthenic fractions; 3) from aromatic hydrocarbons of catalytic-cracking gas oil; 4) specimens; 5) heat of combustion; 6) kcal/kg; 7) kcal/l; 8) density, $\rho_4^{20}$; 9) energy factor, %; 10) temperature of crystallization, °C; 11) kinematic viscosity at -18°, centistokes; 12) fractional composition; 13) 10% boils off, °C; 14) thermostability (filter difference), mm Hg; 15) absent.

synthetically. The hydrocarbons exhibiting high heats of combustion and high density must be included in the composition of such fuels. The isoparaffinic hydrocarbons with compact side groups and some of the naphthenic hydrocarbons with isostructure side chains answer these requirements [8]. Goodman and Wese [9] synthesized hydrocarbons with high energy characteristics from a group of dicyclohexyl derivatives. A comparison of the energy (power) characteristics of these hydrocarbons against the characteristics of other groups of hydrocarbons (Table 179) demonstrated that the energy (power) factors of the former attain 112-113%.

Subsequently, the work proceeded in the direction of the practical derivation, under industrial conditions, of high-energy fuels based on bi- and polycyclic naphthenic hydrocarbons. Conn and Dukcu [sic] [10] derived high-energy fuels based on naphthenic hydrocarbons from the kerosene-gas-oil fractions of select petroleums and from bi- and polycyclic aromatic hydrocarbons of catalytic-cracking gas oil after intense hydrogenation. Table 180 shows the characteristics of certain of these fuels. We can see from the presented data that in terms of the mass heat of combustion these fuels are equivalent to contemporary petroleum VRD fuels; however, in terms of density they exceed substantially the contemporary fuels. In accordance with this, the energy factor of certain of these fuels attains 112.5-115%. Consequently, in using these fuels in jet aircraft we can expect an increase in flight range by 12-15% in comparison with the results obtained on a T-1 fuel. A characteristic feature of these fuels is the high thermal stability at temperatures below 260°. One of the negative characteristics of these fuels is the viscosity which in certain specimens attains 1800 centistokes at -18°.

At the present time, there have been obtained two industrial batches of select high-energy fuels, designated as JP-X [10]. The initial products for the derivation of the JP-X fuels were the aromatic hydrocarbons (primarily, of two-ring structure), separated from catalytic-cracking gas oil, as well as the hydrocarbons obtained from the products of coal processing. These hydrocarbons were subjected to exhaustive hydrogenation to naphthenic hydrocarbons and are, in this form, presently undergoing tests in jet aircraft [11]. The derivation of similar high-energy synthetic fuels is the most promising trend in the development of mass fuels for air-reaction engines (VRD) [10].

## BÖRON-HYDROGEN (BORANE) FUELS

The energy characteristics of the hydrocarbon VRD fuels are limited by the fact that in addition to hydrogen exhibiting the highest heat of combustion of 28,700 $\frac{kcal}{kg}$, these fuels also include carbon whose heat of combustion is not great – 7800 kcal/kg. By replacing the carbon with elements exhibiting higher heating values such as, for example, beryllium (14,970 kcal/kg) and boron (14,170 kcal/kg), great potentials are offered for the production of promising future high-energy VRD fuels.

TABLE 181

Relative Flight Range with Boron-Hydrogen (Borane) Fuels

| 1 Топливо | 2 Относительная дальность полета | 1 Топливо | 2 Относительная дальность полета |
|---|---|---|---|
| JP-4 | 1,0 | Пентаборан 7 | 1,5 |
| JP-4 + 50% бора | 1,2 | Декаборан 8 | 1,5 |
| 3 Бор | 1,4 | Топливо HEF 9 | 1,4 |
| 4 Карбид бора | 1,5 | Алюминий 10 | 1,4 |
| 5 Бериллий | 1,6 | Магний 11 | 0,64 |
| 6 Диборан | 1,6 | Титан 12 | 0,51 |

1) Fuel; 2) relative flight range; 3) boron; 4) boron carbide; 5) beryllium; 6) diborane; 7) pentaborane; 8) decaborane; 9) HEF fuel; 10) aluminum; 11) magnesium; 12) titanium.

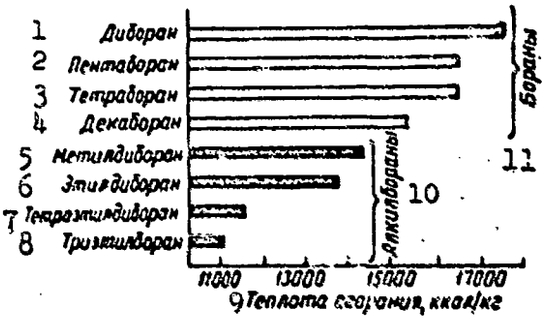


Fig. 233. Heat of combustion of boron-hydrogen (borane) fuels. 1) Diborane; 2) pentaborane; 3) tetraborane; 4) decaborane; 5) methyldiborane; 6) ethyldiborane; 7) tetraethyldiborane; 8) triethylborane; 9) heat of combustion, kcal/kg; 10) alkyl boranes; 11) boranes.

The most accessible are the boron-hydrogen (borane) fuels [12], [13], [14]. The production of fuels based on beryllium is more complex and these exhibit a significant toxic effect.

The basic advantages of the boron-hydrogen (borane) fuels are

that they make it possible:

to increase the engine power and flight range of the aircraft;

to reduce both the volume and weight of the fuel required for the aircraft, without reducing range and flight durations;

to reduce the dimensions and weight of the engine without diminishing the power of the engine.

For example, in designing an aircraft with a given flight range and intended for operation on a boron-hydrogen (borane) fuel, it is possible:

to provide for a lower specific load on the wings;

to reduce the dimensions of the aircraft and increase its speed correspondingly;

to increase the payload of the aircraft;

to increase the operational ceiling and reduce the takeoff run of the aircraft [15].

American boron-hydrogen (borane) fuels are alkylated derivatives of boranes.

The HEF-2 fuel is an alkylated pentaborane, and the HEF-3 fuel is an alkylated decaborane [16, 17, 18]. Ethyl is used as the alkyl radical in these fuels [19]. In addition to the ethylated boranes, a HEF-5 fuel has been developed, and instead of ethyl in this fuel butyl is taken as the alkyl radical. HiCal fuels are alkyl derivatives of diborane [18]. A comparison of these fuels with the hydrocarbon fuel of the wide-fraction JP-4 type in terms of the magnitude of relative flight range of a future aircraft at an altitude of 21 km at a velocity of 3 M shows (Table 181) that HEF-brand fuels make it possible to increase flight range by 40%, and that decaborane and pentaborane make it possible to increase flight range by 50% [20].

The alkyl boranes, although they exhibit a lower heat of combus-

tion (Fig. 233), are nevertheless more stable and less toxic than the nonalkylated boranes.

Much research is being done on diborane, pentaborane, decaborane, and their derivatives. All of the boranes exhibit an unpleasant odor and are toxic. The permissible concentration limit is 0.0001% during 8 hours of work. The vapors of these boranes produce headaches and nausea if inhaled in small quantities. Under general conditions, the boranes are not very stable; however, if special conditions are maintained and air and moisture are kept out, they can be stored for long periods of time.

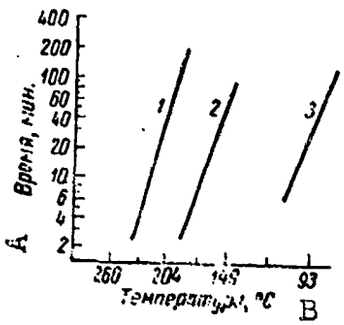


Fig. 234. Thermal stability of 5% solutions of borohydrides. 1) Decaborane; 2) pentaborane; 3) diborane. A) Time, min; B) temperature, °C.

A study of the thermal stability of liquid boranes at various temperatures (Fig. 234) demonstrated that they decompose rapidly with the formation of gaseous products and solid insoluble precipitates. The gaseous products of the decomposition enhance the formation of vapor locks in the fuel system, and the deposits choke the fuel filters. This is the situation, for example, observed in tests on diborane in a standard

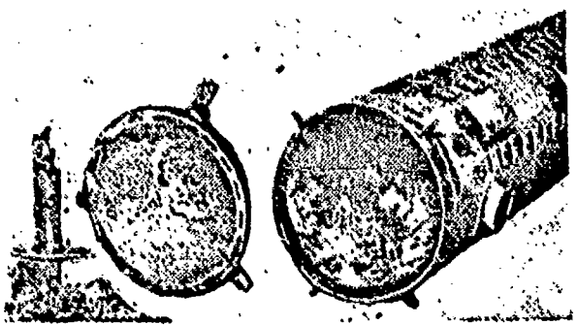

Fig. 235. Deposition of boron oxide in flame tube of TRD combustion chamber.

TRD chamber. The diborane decomposed in the tubing and injectors

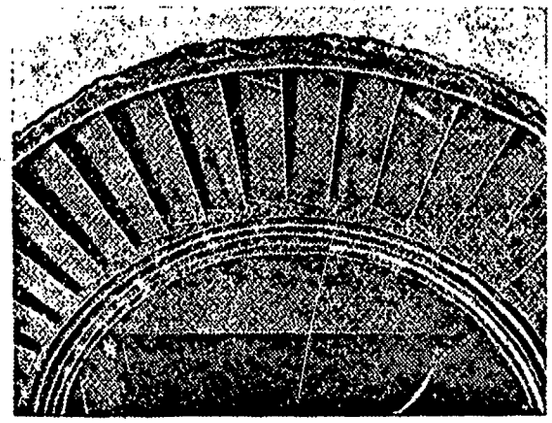

Fig. 236. Deposition of boron oxide on reverse side of TRD turbine stator.

(spray nozzles) of the fuel system, resulting in the partial closing of the nozzles. Deposits of boron oxide quickly formed in the flame tube (Fig. 235). In tests of borane fuels under test-stand conditions in a full-scale turbojet engine, deposition of boron oxide was observed on the walls of the flame tubes, the flame connectors, the stator (Fig. 236) and the rotor of the turbine, and on all component parts of the afterburner and exhaust nozzle (Fig. 237) [20, 21]. Particularly serious difficulties are caused by deposition in gas turbines which, at the present time, are intended for operations close to aerodynamic and mechanical limits. In this respect, the utilization of borane fuels in afterburners involves fewer difficulties. However, in this case, greater attention must be devoted to the thermal stability of the fuel, since the fuel lines of the afterburners are situated in a hotter portion of the engine.

Fig. 237. Deposition of boron oxide on exhaust nozzle of TRD.

With the utilization of borane fuels in afterburners of TRD, the fact should also be borne in mind that the temperature of the exhaust gases must not exceed 1650°. Otherwise, a portion of the heat will be expended on the vaporization of the boron oxide and this reduces the kinetic energy of the exhaust stream which is compensated only by increasing the fuel flow

rate.

There are great potentials for the utilization of borane fuels in ramjet engines. Tests of a ramjet engine operating on pentaborane, under flight conditions, have shown that engine thrust increased approximately by 60% in comparison with operations on a hydrocarbon fuel [20].

Extensive tests of borane fuels have also been carried out in ramjet engines intended for guided missiles. These tests showed that the flight-technical data of these missiles were substantially improved.

In addition to the high heat of combustion the borane fuels exhibit better characteristics of combustion. For example, the speed of flame propagation (diborane – 100 m/sec) is greater by a factor of several tens than in the case of hydrocarbon fuels (0.9 m/sec). In accordance with this, complete combustion of borane fuels in contemporary combustion chambers is achieved over a shorter course than in the case of hydrocarbon fuels. This indicates that in VRD shorter combustion chambers can be employed, and this makes it possible to design a shorter and lighter engine. These concepts are particularly important in the design of ramjet engines where the length of the combustion chamber makes up the basic part of the over-all length of the engine.

A higher speed of flame propagation in the combustion of borane fuels also governs the improvement in the process of flame stabilization as a result of which the combustion may take place at an increased air speed and a shorter diffuser than was required earlier can be used.

METALLOHYDROCARBON FUELS

In addition to increasing the flight range of jet aircraft, ano-

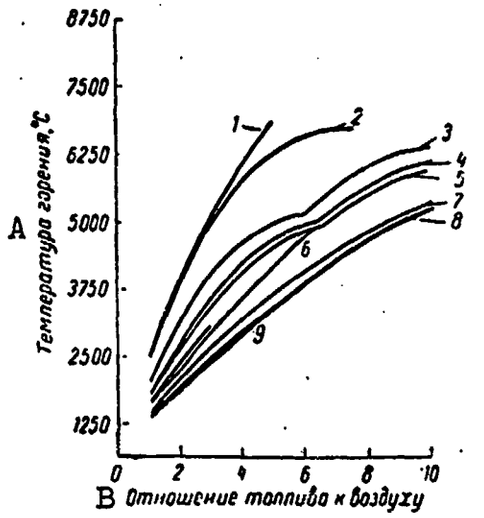


Fig. 238. Temperatures of combustion for metallic fuels and their suspensions in a hydrocarbon fuel. 1) Mg; 2) Al; 3) B; 4) pentaborane; 5) diborane; 6) 50% Mg + + 50% JP-4; 7) $H_2$; 8) JP-4; 9) C. A) Temperature of combustion, °C; B) fuel-to-air ratio.

ther important goal is a pronounced increase in the thrust of VRD. The goal in this case may be achieved by means of fuels which are suspensions of metals in hydrocarbon media. For a pronounced increase in the thrust of air-reaction engines (VRD) a substantial increase in the temperature within the zone of combustion is required. This can be achieved in the combustion of such metals as magnesium, aluminum, boron, or their suspensions in the jet fuel. Figure 238 shows the possible temperatures of combustion for fuels of this type

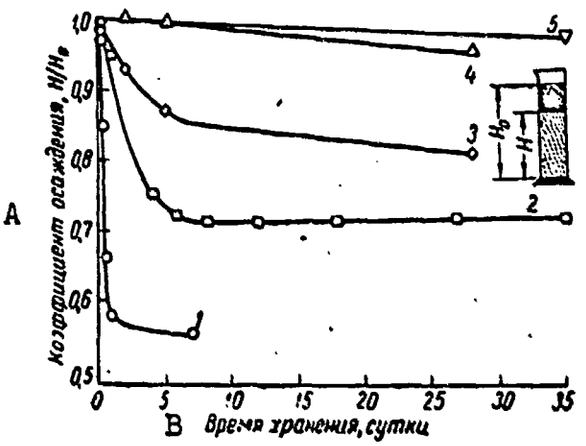


Fig. 239. Effect of additive on stability of 50% magnesium suspensions. 1) Diesel fuel; 2) decane with 1% lecithin; 3) JP-4 with 28% petrolatum; 4) decane with 0.2% lecithin; 5) JP-4 with 52% petrolatum. A) Coefficient of deposition, $H/H_0$; B) storage time, days.

[20]. The highest temperatures are obtained in the combustion of the

oxides of magnesium, aluminum, and boron. A substantial increase in the temperature of combustion is also achieved by using 50% suspensions of the oxides of magnesium and boron in JP-4 fuel.

One difficulty in the utilization of aluminum to obtain suspensions is the fact that as it is burned in the chamber, a sticky low-melting oxide of aluminum is formed and this is deposited on the walls of the combustion chamber and removed only with great difficulty.

Metal suspensions in hydrocarbon fuels must exhibit a relatively high concentration of metal while at the same time exhibiting a viscosity making possible the easy pumping of this suspension through the tubing and providing for ease of atomization through the injectors (spray nozzles). The quantity of metal which can be contained in the suspension is a function of the metal-particle dimensions, the shape of these particles, and the composition of the hydrocarbon medium, as well as of the type and concentration of the stabilizing and thickening additives.

The stability of metallohydrocarbon fuels is a function of the metal-particle dimensions and increases with a reduction in the size of these particles. Stable suspensions of magnesium and boron in a jet fuel can be obtained with a 50-60% metal content, where the particles exhibit a dimension of about 1 μ. For better metal dispersion in suspension surface-active additives, in a 1-2% quantity, are added. Lecithin which is a mixed glyceride of fatty acids (palmitic, stearic, and oleic acids) and phosphoric acid exhibits great effectiveness. In this case, of the three hydroxyls of the phosphoric acid, one forms glycerine ether, and the second forms an ester with the hydroxide of trimethyl-β-oxyethylamine or monoethanolamine. The addition of this additive in a 0.2% quantity, as can be seen from Fig. 239, provides for the adequate stability of the magnesium suspension.

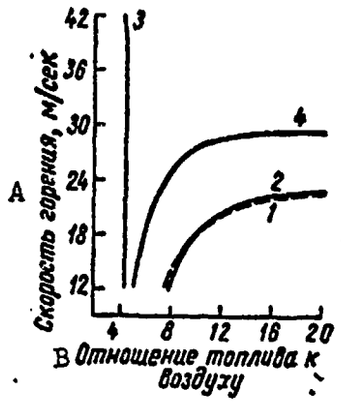


Fig. 240. Burning rate of 50% suspensions of magnesium and boron in JP-4 fuel. 1) JP-4; 2) suspension of boron with particles 1 μ in size; 3) the same, for magnesium; 4) magnesium suspension with particles 15 μ in size. A) burning rate, m/sec; B) fuel-to-air ratio.

In addition to the metal-particle sizes, stability of suspension is greatly affected by the viscosity of the suspensions. The lower the viscosity of the hydrocarbon medium, the more rapidly and in greater quantity the precipitation of metal particles. It is for this reason that in metallohydrocarbon fuels thickening additives such as, for example, petrolatum or the aluminum salt of hexacarboxylic acid are added. Figure 239 shows the effect that petrolatum has on the stability of a magnesium suspension in the JP-4 jet fuel. By means of adding dispersion and thickening additives, it becomes possible to obtain suspensions of magnesium and boron in a hydrocarbon fuel, and these are stable for 30-60 days and more.

The rate and completeness of combustion of metallohydrocarbon fuels is of great importance for an evaluation of these fuels. An estimate of the burning rate of suspensions of boron and magnesium showed (Fig. 240) that the burning rate of the magnesium suspension is substantially greater than that of the boron suspension. For a magnesium suspension, even with particles approximately 20 μ in size, there is more than enough time for complete combustion in ramjet engines and in the afterburners of TRD. A study of the completeness of combustion of boron suspensions in ramjet engines (PVRD) has shown that the completeness of combustion is, on the average, below 85%, and this suspension burns particularly poorly in lean mixtures. On the other hand, the magnesium suspension burned well both in the PVRD and in the af-

terburners of TRD (turbojet engines).

The utilization of magnesium-hydrocarbon suspensions makes it possible to increase markedly the thrust of air-reaction engines. In this case, the thrust augmentation of the engine takes place both as a result of the combustion of the magnesium-hydrocarbon suspension as well as because of the injection of water. The combustion of the magnesium-hydrocarbon suspensions increases the thrust of the engine by 70%, and the additional injection of water increases thrust to 200%. The high effectiveness of the magnesium-hydrocarbon suspensions was confirmed both under test-stand conditions as well as under flight conditions at an altitude of 11.8 km at a velocity of 3.84 M. Magnesium-hydrocarbon suspensions burn well even under conditions in which conventional hydrocarbon fuels of the wide-fraction type burn poorly. Consequently, magnesium-hydrocarbon fuels offer great prospects for increasing the thrust of air-reaction engines (VRD) intended for short-range flying craft.

ORGANOMETALLIC FUELS

Organometallic fuels are also included among the promising fuels for VRD of the future. Of this group of fuels, greatest attention is

| 1 Топливо | 2 Теплота сгорания | |
|---|---|---|
| | 3 ккал/кг | 4 ккал/л |
| 5 Топливо JP-4 | 10300 | 7800 |
| 6 Триэтилалюминий | 10150 | 8400 |
| 7 Триэтилбор | 12400 | 7600 |

1) Fuel; 2) heat of combustion; 3) kcal/kg; 4) kcal/l; 5) JP-4 fuel; 6) triethylaluminum; 7) triethylboron.

being devoted to triethylaluminum, trimethylaluminum, and triethylboron. At the present time, in the USA and Great Britain, these fuels -

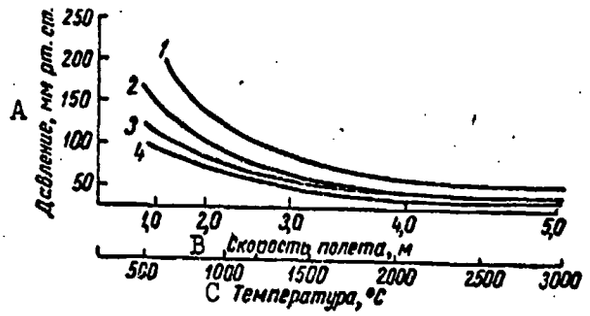


Fig. 241. Lower limit of stable fuel combustion for PVRD (ramjet engines) as a function of flight velocity and pressure in the combustion chamber. Fuels: 1) Petroleum; 2) organometallic; 3) borane; 4) metallohydrocarbon suspension. A) Pressure, mm Hg; B) flight speed, m; C) temperature, oC.

based on aluminum – are being produced in quantities making it possible to use these as starter fuels for air-reaction engines (VRD). For example, in Great Britain triethylaluminum meeting specification DERD-2489 is being used [26].

In addition to its utilization for starter purposes, organometallic fuels can be employed as basic fuels for ramjet engines. We will point out that in terms of energy characteristics these fuels, as can be seen from the figures presented below, differ little from the conventional petroleum JP-4 fuel.

However, these fuels exceed hydrocarbon fuels in terms of combustion characteristics at low pressures within the combustion chamber. Low pressure in the combustion chamber is particularly characteristic of ramjet engines under flight conditions at great altitudes. Under these conditions, the combustion of hydrocarbon fuels is not stable and is frequently accompanied by flame extinction. For example, the combustion of hydrocarbon fuels at a flight velocity of 2 M, as can be seen from Fig. 241, ceases at a combustion-chamber pressure

of 1375 mm Hg, whereas the organometallic fuels burn stably up to pressures of 1000 mm Hg [27]. This results in a substantial increase in the high-altitude capabilities of ramjet engines. For example, if with a hydrocarbon fuel stable combustion in the chamber of a ramjet engine at a flight velocity of 2 M is maintained to an altitude of 21 km, the utilization of organometallic fuels increases the high-altitude performance of the engine under these conditions to 28 km. We can see from Fig. 242 that the utilization of organometallic fuels greatly increases the potentials of using ramjet engines (PVRD) in flights at velocities up to 2-3 M and at altitudes in excess of 10 km. The organometallic fuels are most efficient at flight altitudes between 15-25 km.

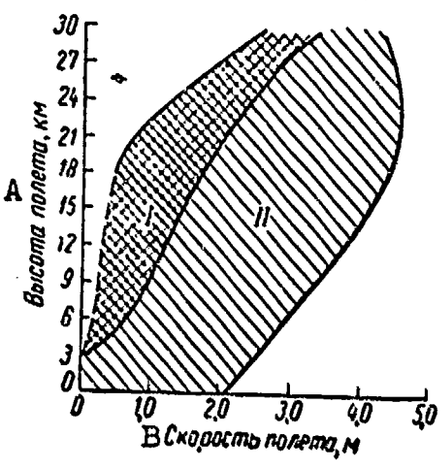


Fig. 242. Expansion of PVRD utilization limits through the utilization of organometallic fuels. I) organometallic fuel; II) hydrocarbon fuel. A) Flight altitude, km; B) flight speed, M.

In addition to the organometallic fuels, as can be seen from Fig. 241, borane fuels based on metallohydrocarbon suspensions also enhance an improvement in combustion in ramjet engines. However, in terms of operational properties, accessibility for production, and in terms of cost, these fuels are significantly inferior to organometallic fuels. It should also be pointed out that in terms of completeness of combustion under high-altitude conditions organometallic fuels are substantially superior to petroleum fuels. Therefore, these fuels are regarded as the most promising fuels of the future, which can be used in ramjet engines (PVRD) in the near future.

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script
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[List of Transliterated Symbols]

769 в = v = vesovoy = mass

769 об = ob = ob'yemniy = volumetric

769 э = e = etalonniy = reference

## Chapter 24

# FUELS FOR LIQUID ROCKET ENGINES

## GENERAL INFORMATION

The radical difference between the rocket engine and all other thermal engines, including the air-breathing jets, consists in the fact that it operates independently of the surrounding medium. This is a highly significant and fundamentally new property in an engine. To burn its combustible, it uses not the oxygen of the air, but a special oxidizer stored aboard the aircraft, or uses as a fuel substances capable of liberating thermal energy and gaseous products as a result of decomposition or other chemical reactions without the participation of an oxidizer. As a result, the rocket engine can operate with the same success both at the surface of the Earth and at high altitudes in a greatly rarefied atmosphere, as well as in airless space and even under water.

The term "fuel" in rocket engineering implies a combination of a combustible and the oxidizer that reacts with it.

The concept embraces substances that are capable of exothermic dissociation or association in the engine with formation of gaseous transformation products without participation of an oxidizer.

The first rocket engines worked on solid fuel – pressed gunpowder. Powder-type rocket engines have been known since remote antiquity. They operate on a simple principle and do so with utter dependability. However, this powder has a low heat of combustion (700-1000 kcal/kg). Moreover, due to the high rate at which the powder

burns and the small quantity that can be carried, the latter limited by the dimensions of the combustion chamber, the operating time of a powder-type rocket engine is very short (0.1 + 25 sec); the thrust developed by the engine is difficult to regulate. Solid-fuel rocket engines are normally used in cases where a one-shot engine of relatively low power and short operating time is required (booster engines, engines for short-range rocket missiles, and so forth).

Konstantin Eduardovich Tsiolkovskiy (1857-1935)

The appearance of liquid-fueled rocket engines, the foundations for whose development were laid by K.E. Tsiolkovskiy [1], opened new prospects for the development of rocket engineering. The heat of combustion of liquid fuels is considerably higher than that of the powders (Table 182). This insures high outflow velocities of the combustion products, and, consequently, makes it possible to develop large thrusts, high speeds and altitudes, and long ranges for the rockets. A liquid-fueled rocket engine can perform for a longer time than a solid-fuel type. Moreover, the use of a liquid propellant makes it possible to control the engine relatively easily by regulating the flow of propellants into the combustion chamber, vary the thrust, and, consequently, control the rocket's flight speed.

K.E. Tsiolkovskiy made a detailed investigation of the heat effects of the combustion reactions of various elements and formu-

TABLE 182

Heats of Combustion of Certain Liquid and Solid Fuels (After K.E. Tsiolkovskiy)

| 1 Жидкие топлива | 2 Количество тепла (в кал), выделяемое при сгорании 1 г стехиометрической смеси с жидким кислородом | 3 Твердые топлива | 4 Количество тепла (в кал), выделяемое при сгорании 1 г вещества |
|---|---|---|---|
| 5 Метан (сжиженный) . . | 2394 | 12 Порох дымный и бездымный . . . . . | 720—960 |
| 6 Этилен (сжиженный) | 2576 | 13 Нитроглицериновый порох . . . . . | До 1195 19 |
| 7 Бензол . . . . . | 2289 | 14 Нитроглицерин . . . . | 1475 |
| 8 Спирт метиловый . . . | 2123 | 15 Пикриновая кислота | 750 |
| 9 Спирт этиловый . . . . | 2327 | 16 Гремучая ртуть . . . . | 350 |
| 10 Эфир . . . . . | 2512 | 17 Динитробензол с азотной кислотой . . . . | 1480 |
| 11 Скипидар . . . . . | 2527 | 18 Алюминий с аммиачной селитрой . . . . . | 1480 |

1) Liquid propellants; 2) quantity of heat (in cal) liberated on combustion of 1 g of stoichiometric mixture with liquid oxygen; 3) solid propellants; 4) quantity of heat (in cal) liberated on combustion of 1 g of the substance; 5) methane (liquefied); 6) ethylene (liquefied); 7) benzene; 8) methyl alcohol; 9) ethyl alcohol; 10) etner; 11) turpentine; 12) black and smokeless powder; 13) nitroglycerine powder; 14) nitroglycerine; 15) picric acid; 16) fulminate of mercury; 17) dinitrobenzene with nitric acid; 18) aluminum with ammonium nitrate; 19) below 1195.

lated the basic requirements for ZhRD fuels [2]. On the basis of his research, he first proposed the use of hydrocarbons, liquid hydrogen, liquid oxygen and, in later studies, oxides of nitrogen and turpentine as fuel components for ZhRD [3]. Tsiolkovskiy was the first to indicate the possibility of using atomic energy in ZhRD, estimated what the results of its mastery would be, and computed the possible exhaust velocities and flight speeds of atomic-fueled rockets [1].

From the day of publication of Tsiolkovskiy's first papers, intensive research began developing both in Russia and abroad with the objective of finding a practical solution to the problem of creating

a liquid-fueled rocket engine. Toward the end of the nineteen-twenties and the beginning of the 'thirties, the first liquid rocket-engine designs made their appearance and the first flights were made with ZhRD-powered flying devices.

Our compatriots V.P. Vetchinkin, Yu.V. Kondratyuk, G.E. Langemak, Yu.A. Pobedonostsev, M.K. Tikhonravov, N.G. Chernyshev, F.A. Tsander and others [4-11] performed monumental theoretical and experimental work toward the creation and investigation of ZhRD rockets and fuels for them.

In 1930-1932, F.A. Tsander built and successfully tested two ZhRD that operated on gasoline/gaseous air and gasoline/liquid oxygen, respectively. F.A. Tsander and Yu.V. Kondratyuk devoted a great deal of attention in their studies to the problems of using metals, which liberate considerably larger quantities of heat on combustion than ordinary combustibles, as fuels; among other things, they proposed that metallic parts of the rocket that became unnecessary after the fuel was burned up be burned in the engine as a secondary fuel [7, 8].

In 1928, Yu.V. Kondratyuk was the first to raise the question of using lithium, boron and their hydrogen compounds and other metals as combustibles, and that of ozone as an oxidizer [8].

In subsequent years, Soviet scientists made a large contribution to the development of ZhRD. Here, they devoted particular attention to the selection of energy sources suitable for use in ZhRD.

The theoretical foundations were worked out for efficient selection of ZhRD fuels, a quality evaluation was given for the most probable propellants as regards their efficiency and the reliability of the engine's operation. In 1930, it was first proposed that the

oxidizer for the ZhRD might be nitric acid, nitrogen tetroxide, or hydrogen peroxide, which subsequently became the most widely used in rocket engineering, or tetranitromethane or perchloric acid. On the basis of theoretical and experimental study, they arrived at the conclusion that of the substances investigated, the most valuable as ZhRD combustibles would be the heavier but not excessively viscous petroleum and lignite-tar distillates, methyl and ethyl alcohols, nitrobenzene, nitrotoluene and certain hydrocarbons.

It was also proposed that a boron-containing colloidal combustible with a high heat of combustion be burned in the engines, and the inherent possibility of using electrical energy in ZhRD was also demonstrated.

N.G. Chernyshev [6] devoted much study to the properties of rocket fuels and to development of methods for producing them under industrial conditions, as well as the combustion processes of various fuels in ZhRD chambers.

Among Western investigators, Eno-Pel'tri (France), Goddard (USA), Oberth and Braun (Germany), Zenger (Austria) [12], and others made essential contributions to the development of rocket engineering.

During the Second World War, the Germans built the powerful (for that time) A-4 (V-2) guided rocket, which had a ZhRD operating on liquid oxygen and ethyl alcohol, a guided antiaircraft rocket and a fighter-interceptor with ZhRD. At the present time, various more highly perfected ZhRD types have been designed and built; these operate on various fuels and develop thrusts ranging from several tens of kilograms to hundreds of tons.

## BRIEF REMARKS ON LIQUID-FUEL ROCKET ENGINES

The liquid-fueled rocket engine may have one chamber (single-chamber ZhRD) or several chambers (multichamber ZhRD). A schematic

diagram of the ZhRD may be found in Figs. 50 and 51 in Chapter 6.

TABLE 183

Illustrative Values of Maximum Attainable Flight Speeds of Aircraft Equipped with Various Types of Engines [14]

| 1 Тип двигателя | 2 Максимально достижимая скорость полета, км/час |
|---|---|
| 3 Поршневые | 600 |
| 4 Турбовинтовые | 900 |
| 5 Турбореактивные | 2 000 |
| 6 Прямоточные ВРД | 6 000 |
| 7 Пороховые ракетные двигатели | 28 000 |
| 8 Жидкостные » » | 50 000 |
| 9 Термоядерные » » | 100 000 |
| 10 Электронные » » | 500 000 |
| 11 Фотонные » » | $300 \cdot 10^3$ |

1) Engine type; 2) top speed, km/hour; 3) piston; 4) turboprop; 5) turbojet; 6) ramjet; 7) solid-fuel rocket engines; 8) liquid-fuel rocket engines; 9) thermal nuclear rocket engines; 10) electron rocket engines; 11) photon rocket engines.

TABLE 184

Specific Fuel Consumption in Various Engines [16]

| 1 Двигатель | 2 На уровне моря | | 5 На высоте 6100 м | |
|---|---|---|---|---|
| | 3 скорость, км/час | 4 удельный расход топлива, кг/кг час | 6 скорость, км/час | 7 удельный расход топлива, кг/кг час |
| 8 Поршневой авиадвигатель | 480 | 0,56 | 600 | 0,71 |
| 9 ТРД | 835 | 1.72 | 835 | 1.46 |
| 10 ЖРД | 1085 | 18,75 | 1100 | 18,75 |

1) Engine; 2) at sea level; 3) speed, km/hour; 4) specific fuel consumption, kg/kg-hour; 5) at 6100 meters; 6) speed, km/hour; 7) specific fuel consumption, kg/kg-hour; 8) reciprocating aviation engine; 9) TRD; 10) ZhRD.

Liquid-fuel rocket engines have been accorded extensive use by virtue of the following special properties and advantages that they possess over other types of engines.

1. The high powers developed by ZhRD, which run to tens of millions of horsepower with a small over-all weight of the engine [13].

Such high powers are not within the capability of any other engine type.

In a VRD, the oxygen of the air used to burn the combustible is diluted to a considerable degree by nitrogen – a ballast element that does not participate in combustion. The oxygen content in liquid oxidizers is considerably higher than that in air, reaching 75-100% of the weight of the oxidizer. As a result, the concentration of chemical energy per unit weight of ZhRD fuel (combustible + oxidizer) is many times larger than in the case of jet fuels. When a ZhRD fuel is burned, a very large quantity of heat is liberated and high temperatures and high combustion-product outflow speeds are attained; this ensures that the engine will deliver high powers.

As a result of the high power, the ZhRD gives the aircraft an extremely high flight speed (Table 183).

2. Design simplicity and low specific weight of the engine, i.e., the weight per 1 kg of thrust. Due to the high thermal stressing, the ZhRD has considerably smaller dimensions and lower weight than other engine types developing the same thrust; this makes its accommodation aboard the aircraft easier.

The specific weights of contemporary ZhRD vary in the range from 0.01 to 0.05 kg/kg of thrust. Thus, for example, in the American "Viking" rocket, it is 0.01, for the "Redstone" it is 0.02, while for the SEPR aircraft ZhRD it is 0.05 kg/kg of thrust [15].

3. The lack of any influence exerted by the environment on engine performance makes it possible for the ZhRD to operate at all altitudes, in airless space and under water.

4. Independence of the ZhRD's thrust of the speed of the flying craft. With increasing altitude, the ZhRD's thrust not only does not fall off, as, for example, it does in VRD, but, on the contrary, in-

creases due to the drop in external pressure.

Higher specific fuel consumption is a distinctive characteristic of the ZhRD. In a ZhRD, the liquid oxidizer is part of the fuel, so that the consumption of fuel per unit of thrust is many times larger in a ZhRD than in reciprocating and turbojet engines (Table 184).

A deficiency of the ZhRD is its short operating time – from 2.5 sec to 2 hours [13]. The high temperature (3000-4000°), pressure (up to 100 atmospheres) and thermal stressing of the combustion chamber (10 to 100 times that prevailing in the VRD), as well as the complexity of providing effective cooling for it are all reasons why the service life of a ZhRD combustion chamber is considerably shorter than that of a VRD.

Also to be included among the shortcomings of the ZhRD are the short operating time of the engine as a result of the high specific fuel consumption.

The above peculiarities of the ZhRD are what determine the range of its expedient application. ZhRD are used where it is necessary to develop high speeds and large thrusts with minimal engine weight.

ZhRD are used as booster powerplants to assist aircraft in taking off, to increase the thrust of sustainer engines briefly in order to reduce climbing time or increase the speed of horizontal flight, as well as in special powerplants.

Rockets with ZhRD are coming into increasingly widespread use for peaceful purposes – for research in the upper layers of the atmosphere and interplanetary space.

The Soviet Union has racked up great successes in the development of rocket engineering. On 4 October 1957, in the Soviet Union, a powerful multistage ballistic rocket was used in the successful launching of the first artificial Earth satellite in history. Launch-

ing of a second and then a third satellite followed in rapid succession. In January 1959, the first Soviet cosmic rocket was launched toward the Moon and became an artificial planet. In September of 1959, a Soviet cosmic rocket was the first in history to reach the surface of the Moon, and in October of the same year an automatic interplanetary station was placed on trajectory for a flight around the Moon. Subsequently, three powerful satellite-spacecraft were launched into orbit around the Earth and the problem of safe return of satellites to the Earth was successfully solved for the first time. Finally, on 12 April 1961, the Soviet citizen Major Yu.A. Gagarin became the first man in history to complete a cosmic flight. The USSR took a firm grip on the leading position in the world in the field of rocket building.

REQUIREMENTS IMPOSED ON ZhRD FUELS

Selection of the fuel is an extremely important stage in the process of designing a ZhRD. The efficiency with which the ZhRD performs and the speed, range and altitude of the rockets depend in many respects on the fuel employed. The history of ZhRD development is, to a considerable degree, the history of searches for and tests of liquid materials suitable for combustion in the engine's chamber that will ensure its efficient operation. A large number of chemical substances was studied. However, in view of the special requirements made as regards the quality of the fuels, only a relatively small number of them have been used in practical rocket engines.

The specifications for ZhRD fuels are determined on the basis of the need to guarantee economical engine operation, easy starting, stable combustion of the fuel, effective cooling of the combustion chamber, trouble-free operation of the fuel-feed system, operational reliability under various conditions, and convenience and safety in

handling the fuels during storage and shipping.

Engine Economy

In terms of insuring the highest possible operating economy of the engine, the effectiveness of a fuel is normally evaluated by the effective outflow speed of its combustion products. According to the theory of jet propulsion, the thrust of a rocket engine may be expressed by the equation

$$R = mu, \tag{1}$$

where R is the reaction thrust of the engine in kg, m is the mass of fuel burned in the engine in 1 sec or the mass of the gaseous combustion products of the fuel that flow out through the engine nozzle in 1 sec, in $kg \cdot sec^2/m$, and u is the outflow speed of the combustion products in m/sec.

Expressing the mass m in terms of weight, Equation (1) may be presented in the following form:

$$R = \frac{G}{g} u, \tag{2}$$

where G is the per-second fuel consumption in kg and g is the acceleration of gravity in $m/sec^2$.

The higher the per-second consumption (of mass) of the fuel burned in the engine and the higher the outflow speed of the combustion products of the fuel, the greater will be the reaction thrust developed by the engine. Consequently, obtaining a high reaction thrust requires selection of fuels that have high combustion rates in the engine and enable us to obtain the highest possible combustion-product exhaust velocity.

The outflow speed of gaseous combustion products from a ZhRD nozzle may also be determined with the aid of the following mathematical relationships:

$$u = \sqrt{\eta_t 2g \frac{K}{K-1} PV} \qquad (3)$$

or

$$u = \sqrt{\eta_t 2g \frac{K}{K-1} RT}, \qquad (4)$$

where P is the gas pressure in the combustion chamber, V is the volume of the gases liberated on combustion of 1 kg of fuel (under standard conditions) or the specific volume of the gases, T is the combustion temperature of the fuel, R is the gas constant of the combustion products, which depends on the composition of the gases, K = $= C_P/C_V$ is the adiabatic exponent, which depends on the composition of the combustion products and the temperature of the gases, and $\eta_t$ is the thermal efficiency of the engine or the fraction of the fuel's heat energy that is converted into mechanical energy.

The primary conclusion to be drawn from Equations (3) and (4) is that the exhaust velocity of the combustion products increases with increasing specific volume of the gases (gas evolution) and the combustion temperature of the fuel, and depends on the gas constant R.

The combustion temperature of the gases is generally determined by the heat of combustion of the fuel, and the gas constant by the composition of the combustion products, since

$$R = \frac{848}{\mu},$$

where $\mu$ is the apparent molecular weight of the fuel's combustion products.

The gas constant R characterizes the work capacity of the gas and increases as its molecular weight diminishes. Consequently, to obtain a high outflow velocity of the combustion-product gases, the fuels must have the lowest possible molecular weight.

The concept of "specific thrust" ($R_{ud}$), i.e., the thrust of the

engine referred to the unit per-second fuel consumption, is normally used to characterize a fuel. The specific-thrust value may be computed with the aid of the following equations, which were derived by V.P. Glushko [5] assuming that the heat energy of the fuel is converted into kinetic energy of the combustion products:

$$R_{уд} = 9{,}33\sqrt{\eta_t H} \text{ kg-sec/kg};$$
$$R_{уд} = 9{,}33\sqrt{\eta_t H \varrho} \text{ kg-sec/liter},$$

where H – the heat of combustion of the fuel – is the quantity of heat liberated on complete combustion of 1 kg of fuel less the heats of condensation of the substances, in kcal/kg, $\rho$ is the density of the fuel in kg/liter and $\eta_t$ is the thermal efficiency of the engine.

The higher the heat of combustion and density of the fuel, the higher will be the engine's specific thrust. And in turn, the higher the engine's specific thrust, the lower will be the fuel consumption per 1 kg of thrust for a given absolute thrust and, consequently, the longer will be the range of the apparatus for a given fuel supply in the tanks.

We note here that for ordinary combustibles, with which atmospheric oxygen is used as the oxidizer, the heat of combustion is conventionally referred only to the weight of the combustible itself. In ZhRD, the combustible and oxidizer are accommodated in tanks aboard the rocket craft, so that the heat of combustion of rocket fuels is referred to the weight of the entire fuel; combustible + + oxidizer. Here, the proportions of combustible and oxidizer are assumed to be stoichiometric.

Figure 244 shows how the specific thrust of an engine varies as a function of the heat of combustion of the fuel for fuels of different densities. It will be seen from Fig. 244 that a given specific-thrust value may be obtained either by using a fuel of low density

(0.5 kg/liter) and a high heat of combustion (4000 kcal/kg) or by using a fuel with a lower heat of combustion (2000 kcal/kg) but a high density (1.0 kg/liter).

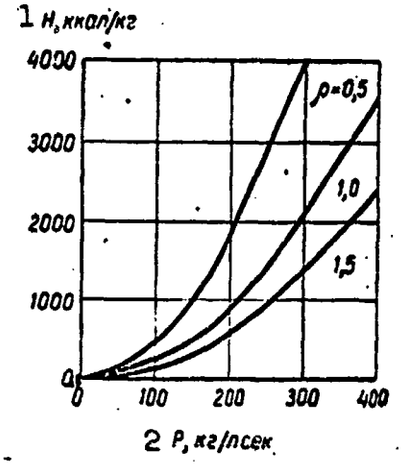


Fig. 244. Variation of specific thrust $R_{ud}$ of ZhRD as a function of heat of combustion H and density ρ of fuel. 1) H, kcal/kg; 2) P, kg/liter-sec.

This type of relationship between the heat of combustion and the density of a fuel becomes understandable if we remember that the specific thrust of the engine depends on the quantity of combustion products formed on combustion of a unit amount of fuel and on their temperature.

For a given heat of combustion, the quantity of products formed increases as the density of the fuel rises. A consequence of an increase in heat of combustion is an increase in the temperature of the combustion products. In either case, we observe an increase in the engine's specific thrust.

It should be noted, however, that the range of a rocket depends on the manner in which the engine's specific thrust is increased. If the engine's specific thrust is increased by raising the heat of combustion, the range of the rocket will increase in proportion to the fuel's heat of combustion. If the engine's specific thrust is increased by raising the density of the fuel, the total weight of the rocket will increase, and this will absorb an additional amount of the specific-thrust gain achieved. Consequently, increasing the range of the rocket by a given amount requires a relatively larger increase in fuel density rather than in its heat of combustion.

As will be recalled from thermodynamics, the thermal efficiency of the engine ($\eta_t$) depends on the adiabatic exponent K, the ratio

$C_p/C_V$), which is determined by the composition of the fuel's combustion products. As we pass from monatomic to polyatomic gases, $\eta_t$ diminishes (Table 185).

To achieve a high specific thrust, the fuel's combustion products must be stable against thermal dissociation. Dissociation of the combustion products is accompanied by absorption of energy, and this reduces the amount of heat evolved in the ZhRD's combustion chamber.

The extent to which the combustion products dissociate increases with increasing temperature. Consequently, it is desirable to have the lowest possible temperature in the combustion chamber in order to reduce the heat-energy losses due to dissociation of the combustion products.

For a given fuel heat of combustion, the combustion temperature and, consequently, the degree of dissociation of the combustion products will be the smaller the larger their unit-weight heat capacity. A reduction in the combustion-product molecular weight results in an increase in their heat capacity and, consequently, in a drop in the fuel's combustion temperature.

TABLE 185

Thermal Efficiency of Rocket Engine as a Function of Composition of Fuel Combustion Products

| 1 Число атомов в молекуле газа | 2 Химическая формула продуктов сгорания | K | $\eta_t$ при давлении в камере сгорания, ат 3 | | |
|---|---|---|---|---|---|
| | | | 25 | 50 | 100 |
| 1 | H | 1.667 | 0.724 | 0.791 | 0.842 |
| 2 | CO; $N_2$ | 1.286 | 0.511 | 0.543 | 0.641 |
| 3 | $CO_2$; $H_2O$ | 1.167 | 0.369 | 0.422 | 0.482 |
| 4 | $BF_3$ | 1.111 | 0.276 | 0.297 | 0.369 |
| 5 | $SiF_4$; $B_2O_3$; $Al_2O_3$ | 1.063 | 0.219 | 0.269 | 0.298 |

1) Number of atoms in molecule of gas; 2) chemical formula of combustion products; 3) $\eta_t$ at combustion-chamber pressure in atmospheres.

The degree of combustion-product dissociation depends on the

number of atoms in the gas molecule. Molecules with smaller numbers of atoms are more stable against thermal dissociation than molecules with large numbers of atoms.

The effective efficiency ($\eta_e$) of the engine, which is characterized by the ratio of the quantity of heat converted into kinetic energy to the total amount of heat expended, influences specific thrust. The effective efficiency of an engine depends on the completeness with which the fuel is burned. The higher the completeness of fuel combustion, the more heat will be converted into kinetic energy, i.e., the higher will be the engine's effective efficiency.

For a given set of design parameters, the completeness with which the fuel is burned and, consequently, the effective efficiency of the engine depend to a considerable degree on fuel quality and primarily on such physicochemical properties as the concentration range of ignition, the ignition lag, the normal rate of flame propagation and vaporizability.

Evaporating and mixing in the ZhRD, the atomized combustible and oxidizer form zones of widely varying composition – from very rich to very lean mixtures. The wider the concentration range of ignition exhibited by the fuel, the greater will be the number of combustion foci that appear and the higher will be the mass rate of combustion, the per-second fuel consumption and the completeness of fuel combustion.

In the engine's chamber, the fuel does not ignite instantaneously after sparking or after hypergolic components have been brought into contact, but only after a certain interval of time has elapsed – the ignition lag.

The ignition lag influences the completeness of a fuel's combustion. With a long ignition lag, the fuel modules travel greater

distances in the combustion chamber before they burn. When this happens, the time available for combustion of the fuel is reduced accordingly and the amount of fuel burned after leaving the nozzle will increase.

Substances of various types that frequently differ considerably as regards normal rate of flame propagation may be used as combustibles and oxidizers for ZhRD.

The higher the normal velocity of flame propagation, all other conditions the same, the more complete will be combustion of the fuel in the engine. Finally, completeness of combustion depends on the vaporizability of the fuel components – the combustible and the oxidizer.

Vaporization of the fuel is a necessary condition for its combustion. Before igniting, the fuel must be vaporized and mixed with an oxidizer. Consequently, if the vaporizability of the fuel or of one of its components lies below a certain limit, the completeness of fuel combustion will be reduced.

The evaporation rate of the fuel components in the engine depends not only on their physical properties, but also on the fineness with which they are atomized. As the droplet diameter diminishes, the rate of vaporization rises. The fineness of atomization is, in turn, the greater the smaller the surface tension of the combustible and the oxidizer.

Consequently, to ensure economical operation of a ZhRD, the fuel must be characterized by the highest possible heat of combustion and density, wide concentration ranges of ignition, a minimal ignition lag, a high normal flame-propagation velocity, low surface tension and a rather high vaporization rate of its components. The gaseous combustion products of the fuel must have the lowest possible molecu-

lar weight.

Starting the Engine

The operating dependability of an engine depends in many respects on how it is started. At the instant of starting, the fuel is ignited after an interval of time equal to the ignition lag. During this time, an explosive mixture, instantaneous ignition of which results in an explosion, accumulates in the combustion chamber. The force of the explosion depends on the quantity of fuel that has entered the combustion chamber by the time of ignition. With long ignition lags, so much fuel may accumulate in the combustion chamber that its ignition would result in damage to the engine.

The smaller the amount of fuel that has entered the chamber prior to ignition, the more smoothly will the engine start.

The quantity G of fuel that has entered the combustion chamber by the time of ignition depends, on the one hand, on the fuel-feed rate Q and, on the other hand, on the ignition lag $\tau$:

$$G = Q\tau.$$

It follows from this that the fuel-flow rate should be smaller than its maximum and the ignition lag should be as short as possible when the engine is started. To a certain degree, the ignition lag characterizes the starting properties of the fuel.

The ignition lag depends on mixture composition. At the time of starting, many zones with rich and lean combustible-and-oxidizer mixture form in the combustion chamber. Consequently, one of the requirements set forth for a ZhRD fuel is constancy of the fuel's ignition lag with respect to mixture composition with a relatively low absolute magnitude of this value.

The ease of ignition of a fuel depends to a considerable degree on the concentration ranges and ignition temperature of the fuels. The

wider the concentration range of ignition of a fuel, the easier will it be to start the engine. In this case, a large number of zones in which the combustible-to-oxidizer ratio is within the ignition range will form in the combustion chamber.

It is also obvious that the ease and dependability of starting will be the greater the lower the fuel's ignition temperature. The latter depends on the vaporizability of the fuel.

Consequently, to ensure dependable starting of a ZhRD it is necessary that the fuel be characterized by the shortest possible ignition lag, wide concentration ranges of ignition, and rather good vaporizability, the latter guaranteeing formation of the necessary concentration of combustible and oxidizer vapors in the cold engine at the time of starting.

Stability of Combustion of Fuel in ZhRD

One of the requirements set forth for ZhRD is that it guarantee a constant thrust for a given fuel-flow rate. This requirement is never satisfied in practice. There are always pressure fluctuations at a frequency ranging from 10 to 5000 cycles in the engine's combustion chamber, and these sometimes become aperiodic. The pulsations of engine thrust that arise as a result may lead to damage to components of the vehicle and even to the engine itself.

Such pressure oscillations are related to the fuel's ignition lag. With an adequate pressure prevailing in the fuel-feed line, variations in the combustion-chamber pressure result in corresponding variations in the quantity of fuel fed. Thus, when the combustion-chamber pressure rises, the fuel-feed rate diminishes. In turn, the drop in fuel-feed rate reduces the combustion-chamber pressure; however, this response does not take place instantaneously in the engine, but only after a certain interval of time has elapsed, and this time

depends on the ignition lag. During this time, the pressure continues at its elevated level and the fuel-feed rate is subnormal. Then the process is repeated in reverse order. Due to the depressed pressure in the combustion chamber, the fuel-feed rate rises and this raises the pressure in the combustion chamber. In this case, the pressure, which has again been raised as a result of the fuel's ignition lag, is maintained in the combustion chamber longer than is required to equalize the pressure and the fluctuations do not die out. Obviously, the shorter the ignition lag of the fuel, the higher will be combustion stability, the lower will be the amplitude of the oscillations, and the more dependably will the engine perform.

Stable combustion of fuel in a ZhRD depends not only on the fuel's ignition lag, but also on the engine's design and operating parameters. Research has shown that to ensure stable operation it is necessary to:

a) increase the pressure difference between tank and chamber;

b) increase the combustion-chamber volume and the length of the pipelines;

c) reduce the cross section of the pipelines or increase the mass flow rate in them [17].

Obviously, in addition to the design parameters, the quality of the fuel and such indices as viscosity and density in particular may influence the pressure difference between the tank and the chamber and the mass flow rate in the fuel lines.

Under the operating conditions of ZhRD, the temperature of the fuel in the tanks may vary over a wide range – from –50 to +50° and more – as a function of ambient temperature. The viscosity and density of the fuel will vary accordingly. The higher the temperature of the fuel, the lower will be its viscosity and the hydraulic resistance

in the fuel line; this will be reflected in a drop in the pressure difference between the tank and the chamber.

Simultaneously with an increase in the temperature of the fuel, the density of the components diminishes and the mass flow rate in the pipelines drops accordingly. Consequently, reducing viscosity and density contributes to lowering the stability of combustion.

However, these quality indices of the fuel have less influence on the operating stability of a ZhRD than does the ignition lag. Consequently, the fuel must be characterized primarily by a minimal ignition lag if stability of combustion in a ZhRD is to be ensured.

Cooling of ZhRD Combustion Chambers

The ZhRD is an apparatus operating under very high thermal stress. A large quantity of fuel is burned in its relatively small volume in a very short time.

Reliable operation of a ZhRD requires sufficiently effective cooling of the engine's combustion chamber and nozzle. The quantity of heat that passes through the cooled walls of the nozzle may reach very high values (over $5 \cdot 10^6$ kcal/$m^2$-hour). Here, the difference between the temperatures on either side of the wall may reach 500-600°.

ZhRD are cooled either by pumping combustible or oxidizer through a coolant jacket on their way to the engine's nozzles (regenerative cooling) or by forming a thin film of combustible or oxidizer on the inner surface of the combustion chamber and nozzle, so that, on evaporation, it will protect the walls by reducing the quantity of heat supplied to them by the combustion products (film cooling).

Sometimes combined cooling is employed: regenerative + film.

Additional requirements are imposed on fuel components if they are to be used as coolants. Foremost among these are adequate thermal stability.

The effectiveness of regenerative cooling depends on the boiling point and heat capacity of the coolant. The higher these indices, the greater the amount of heat that 1 kg of coolant can absorb and the more effective the cooling. The effectiveness of film cooling of an engine depends on the heat of vaporization of the coolant, in addition to the indices enumerated above. Obviously, the higher the heat of vaporization of the coolant, the more effectively will it cool the engine.

Consequently, the components of fuels (or at least one of them) must be characterized by a high boiling point and high values of heat capacity and latent heat of vaporization.

Moreover, the fuel's components must have low saturation vapor pressures and not corrode the metal of the engine's liner at elevated temperatures.

Fuel Feed into ZhRD Combustion Chamber

A necessary condition for dependable operation of a ZhRD is utterly dependable fuel supply to the combustion chamber. Causes of fuel-supply trouble in the liquid rocket engine that depend on fuel quality may be a high pour point of the fuel components, high vapor pressure, which creates a danger of vapor-lock formation, and inadequate chemical stability.

Formation of tarry substances and deposits that interfere with normal operation of the ZhRD may be among the consequences of inadequate chemical stability in certain types of combustibles. The specifications for chemical stability of the combustible become more rigid if it is used as a coolant. At elevated combustible temperatures, in the coolant jacket, tarry substances may form and settle to cause local deterioration of heat dissipation and, possibly, burn-through of the combustion chamber.

Moreover, the use of a chemically unstable combustible sometimes causes formation of scale on the fuel nozzles and in the combustion chamber; this is detrimental to atomization, interferes with combustion, and may even lead to burnout of the combustion chamber.

Other Specifications Set Forth for Fuels

The components of a fuel – combustible and oxidizer – may be stored for long periods, pumped and shipped before they arrive at the engine's combustion chamber.

During this time, such factors as temperature, contact with oxygen and moist air and various metals, intensive agitation during transfers, etc., act upon the combustible and oxidizer. The combustible and oxidizer may undergo no changes in their physicochemical indices under these conditions.

The requirement of high physical stability imposed upon the combustible and oxidizer is dictated by the effort to use substances that do not admit of large evaporation losses during storage and shipping. The combustible and oxidizer must exhibit chemical stability adequate to exclude the possibility of slow or explosive decomposition during storage and transportation. The use of certain rather unstable, easily decomposed substances as fuel for ZhRD or fuel components makes it more difficult to use them.

In addition to adequately high physical and chemical stability, it is desirable that the components of a ZhRD fuel be safe to handle and not represent a fire or toxicity hazard and be available on an industrial scale.

At the present time, there are no fuels that fully satisfy all of the specifications set forth for them. In practice, it is necessary to select for use fuels that will give the best results for a given set of ZhRD working conditions.

## CLASSIFICATION OF FUELS FOR ROCKET ENGINES

Fuels for rocket engines may be classified on the basis of various criteria. On the basis of physical state, they are classified as liquid and solid fuels (powders).

Liquid fuels are subdivided into two classes in accordance with the method in which they are used: the bipropellant and monopropellant types (Fig. 245). Here the term "propellant" applies to each of the substances fed separately into the ZhRD combustion chamber.

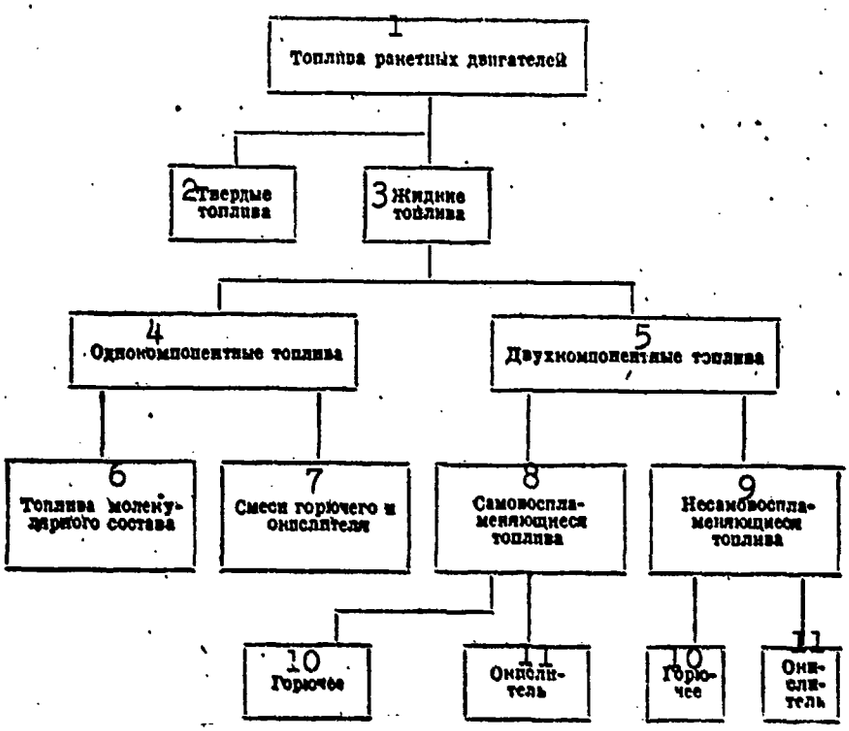


Fig. 245. Classification of fuels for rocket engines. 1) Rocket-engine fuels; 2) solid fuels; 3) liquid fuels; 4) monopropellant fuels; 5) bipropellant fuels; 6) molecular-composition fuels; 7) mixtures of combustible and oxidizer; 8) hypergolic fuels; 9) nonhypergolic fuels; 10) combustible; 11) oxidizer.

As the name indicates, bipropellant fuels consist of two propellants — the combustible and the oxidizer — that are fed separately into the engine's chamber. These propellants are mixed in the ZhRD's combustion chamber. Such fuels are also known as separately-fed fuels.

Monopropellant fuels are those that require no externally [illegible]

plied oxidizer for combustion. The use of monopropellant fuels makes it possible to simplify the engine's fuel system considerably. However, their use is as yet limited by the explosion hazards that they create and their relatively low heats of combustion.

Bipropellant fuels are most widely used.

Separate storage of the combustible and oxidizer in different tanks greatly reduces the explosion hazard and ameliorates the conditions of use, storage and shipping of the fuel. Moreover, the use of bipropellant fuels expands considerably the possibilities for selecting substances suitable for use as the combustible and oxidizer and thus enables us to create the most effective fuel mixtures.

Bipropellant fuels may be broken down into two groups on the basis of the method of ignition in the engine: hypergolic and nonhypergolic fuels.

On contact between certain combustibles and oxidizers at normal temperature, a chemical reaction takes place with evolution of a quantity of heat adequate to ignite the fuel mixture. Such fuels have come to be known as hypergolic.

The second group of fuels includes those whose liquid components (combustible and oxidizer) do not ignite on contact and require an extraneous source of heat for their ignition. Engines that operate on such fuels must be equipped with devices to fire the fuel mixture.

The advantages of forced-ignition fuels include a considerable reduction of the fire hazard. If the combustible and oxidizer are [accidentally] poured together, their contact does not result in a conflagration in the absence of an ignition source.

A very large number of combinations of different substances may be used as forced-ignition bipropellant fuels.

On the basis of their principal functions, ZhRD fuels are classed

as sustaining, starting and auxiliary.

The sustaining fuels are the fuels used directly to operate the engine as the basic energy source and working fluid.

The starting fuels are fuels used for ignition of nonhypergolic sustainer fuels in the combustion chamber when the engine is started.

The auxiliary fuels include fuels used to feed the ZhRD's auxiliary equipment (turbopump set, liquid pressure accumulator of system feeding sustainer fuel, and so forth).

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[List of Transliterated Symbols]

800 yд = ud = udel'nyy = specific

## Chapter 25

## COMBUSTIBLES FOR LIQUID ROCKET MOTORS

Various compounds and mixtures may be used as combustibles for ZhRD. A combustible is preferably evaluated according to its heat of combustion with a given type of oxidizer, the ignition time lag, the concentration limits for ignition and other indices that characterize its energy and operating properties.

Exactly the same combustible may form a hypergolic combination with one oxidizer and a nonhypergolic with another.

We may classify combustibles for ZhRD into the following groups according to chemical composition:

hydrocarbons and their mixtures (gasoline, ligroin, kerosene);

alcohols (methyl, ethyl, furfuryl, etc.);

amines ( aniline, triethylamine, xylidine, etc., and their mixtures);

hydrazine and its derivatives (hydrazine hydrate, dimethylhydrazine, etc.).

In addition, liquid ammonia, liquid hydrogen, various metals and their compounds, and other substances can be used as combustibles.

The basic physical and chemical characteristics of certain compounds finding application as ZhRD combustibles are shown in Table 186 [1].

### HYDROCARBON COMBUSTIBLES

Hydrocarbon combustibles obtained from petroleum are the cheapest of all known combustibles, and are supplied by the broadest assor-

material base. Naturally, this has drawn the attention of researchers to this type of combustible even before the period in which rocket technology developed. The first fuel mixtures employed in ZhRD were oxygen-gasoline mixtures [7].

A high heat of combustion characterizes hydrocarbon combustibles. This positive property of hydrocarbons was an obstacle to their practical utilization in the early period of ZhRD development. Owing to the high heat of combustion of hydrocarbons very high temperatures appear in the combustion chamber; this complicates the selection of structural materials that will resist such temperatures.

For this reason, it is especially difficult to burn hydrocarbons with liquid oxygen. It is a very complicated matter to cool an engine with a hydrocarbon combustible, since the proportion of combustible in the fuel mixture is relatively small (20%), while the heat capacity of the hydrocarbons is also small (~0.45 kcal/kg). Liquid oxygen is little suited to cooling an engine owing to its low boiling point.

Engine designs presently exist that make it possible to use hydrocarbon combustibles with either liquid oxygen or with oxidizers based upon nitric acid and hydrogen peroxide [8, 18]. The ZhRD in many large ballistic rockets of the United States operate with hydrocarbon combustibles.

The various hydrocarbons contained in petroleum products differ little among themselves in heat of combustion (Table 187) and ignition lag (Fig. 246); the choice of combustible hydrocarbon composition is thus normally made so as to satisfy requirements for other characteristics as far as possible.

As a rule, ZhRD use aviation kerosene, cracked kerosene, gasoline, and other products resulting from the processing of petroleum, coal,

TABLE 186

Basic Physical-Chemical Properties of some ZhRD Combustibles

| 1 Горючее | 2 Химическая формула | 3 Молекулярный вес | 4 Температура кипения, °C | 5 Температура замерзания, °C | 6 Плотность в жидком состоянии $\rho_4^{20}$ | 7 Вязкость, сантипуазы |
|---|---|---|---|---|---|---|
| 8 Бензин | $C_{7,1}H_{15}$ (26 средняя) | 26 100,0 (средний) | 40—180 | 27 Ниже —60 | 0,69—0,74 | 0,26 (93°) |
| 9 Керосин | $C_{10,7}H_{20}$ (26 средняя) | 26 150,0 (средний) | 150—315 | 27 Ниже —50 | 0,79—0,84 | 1,5—2,0 (20°) |
| 10 Ацетилен (жидкий) | $C_2H_2$ | 26,04 | 83,6 | —81,5 | 0,613 * | — |
| 11 Толуол | $C_7H_8$ | 92,13 | 110,6 | —95,0 | 0,867 | 0,59 (20°) |
| 12 Изооктан | $C_8H_{18}$ | 114,22 | 99,2 | —107,4 | 0,692 | 0,50 |
| 13 Метиловый спирт | $CH_3OH$ | 32,03 | 64,6 | —94,9 | 0,781 | 0,55 |
| 14 Этиловый спирт | $C_2H_5OH$ | 46,07 | 78,3 | —114,0 | 0,789 | 1,20 |
| 15 Фурфуриловый спирт | $C_4H_3OCH_2OH$ | 98,10 | 171,0 | —32 | 1,128 | 8,10 ($10^3$) |
| 16 Анилин | $C_6H_5NH_2$ | 83,02 | 184,4 | —6,2 | 1,020 | 6,60 (10°) |
| 17 Этиламин | $(C_2H_5)_2NH$ | 73,14 | 56 | —50 | 0,700 | — |
| 18 Триэтиламин | $(C_2H_5)_3N$ | 101,07 | 90,0 | —115 | 0,728 | — |
| 19 Ксилидин | $(CH_3)_2C_6H_3NH_2$ | 121,19 | 216,0 (728 мм 28 рт. ст.) | —54 | 0,798 | — |
| 20 Гидразин | $N_2H_4$ | 32,05 | 113,5 | 2 | 1,010 | 1,00 (27°) |
| 21 Гидразингидрат | $N_2H_4 \cdot H_2O$ | 50,06 | 118,0 | —52,0 | 1,030 | — |
| 22 Диметилгидразин | $(CH_3)_2N_2H_2$ | 62,12 | 63 | —58 | 0,830 | 0,51 (25°) |
| 23 Аммиак (жидкий) | $NH_3$ | 17,03 | —33,4 | —77,7 | 0,817 * | 0,27 (60°) |
| 24 Винилбутиловый спирт | $C_4H_3OCH_2OH$ | 98,10 | 171,0 | —32,0 | 1,128 | 8,10 (10°) |
| 25 Водород (жидкий) | $H_2$ | 2,02 | —253 | —259 | 0,070 * | 0,02 (—259°) |

*Density at boiling point.

1) Combustible; 2) chemical formula; 3) molecular weight; 4) boiling point, °C; 5) freezing point, °C; 6) density as a liquid, $\rho_4^{20}$; 7) viscosity, centipoises; 8) gasoline; 9) kerosene; 10) acetylene (liquid); 11) toluene; 12) isooctane; 13) methyl alcohol; 14) ethyl alcohol; 15) furfuryl alcohol; 16) aniline; 17) ethylamine; 18) triethylamine; 19) xylidine; 20) hydrazine; 21) hydrazine hydrate; 22) dimethylhydrazine; 23) ammonia (liquid); 24) vinylbutanol [sic; formula and characteristics are the same as those listed for furfuryl alcohol]; 25) hydrogen (liquid); 26) average; 27) below; 28) mm Hg.

and shales. Preference is most frequently given to the kerosenes, which have greater density than the gasolines, and which are nearly as good with respect to other characteristics (Fig. 247). Kerosenes, which boil at higher temperatures, may be used to cool the engine.

In the ZhRD for the American Nike and Atlas rockets, standard JP-4 aviation fuel is used as the combustible (this is a mixture of gasoline and kerosene fractions [11 - 12]).

In recent years, grade RP-4 kerosene has been introduced specially in the United States for ZhRD (specification Mil-R-25576); it has a

TABLE 187

Heat of Combustion for Various Classes of Hydrocarbons in Stoichiometric Mixture with Liquid Oxygen

| 1 Углеводороды | 2 Теплота сгорания, ккал/кг |
|---|---|
| 3 Парафиновые . . . . . | 2250—2280 |
| 4 Олефиновые . . . . . | 2250—2400 |
| 5 Нафтеновые . . . . . | 2250—2290 |
| 6 Ароматические . . . . . | 2280—2300 |

1) Hydrocarbons; 2) heat of combustion, kcal/kg; 3) paraffin; 4) olefins; 5) naphthenes; 6) aromatics.

very low content of aromatic and unsaturated hydrocarbons, and boils in the 195 – 275° range. It is used with nitric acid or with liquid oxygen in the engines of the Thor rocket, and in the first stages of the Vanguard and Saturn rockets [8, 12].

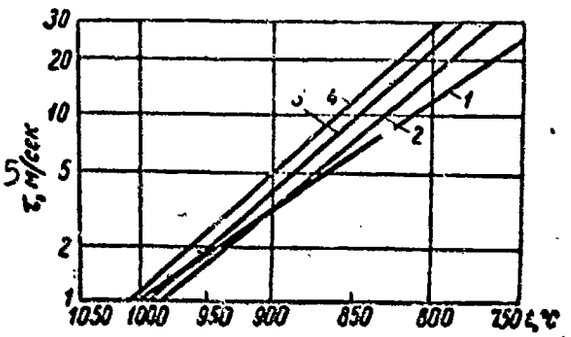



Fig. 246. Variation in ignition lag of hydrocarbons mixed with air as a function of temperature [52]. 1) Ligroin, d(15/15) = 0.721; 2) fractions boiling in 100 – 120° range, d(15/15) = 0.743; 3) kerosene, d(15/15) = 0.743; 4) heavy fuel, d(15/15) = 0.875; 5) τ, m/sec.

When kerosene is used to cool an engine chamber whose walls are heated to high temperature (300 – 600°), it is possible that solid deposits will form on the cooled surfaces, considerably impairing cooling conditions. The fraction composition of RP-1 kerosene has been so calculated as to reduce the content of cyclic (naphthene) hydrocarbons which as investigations have shown [13] possess a higher thermal stability.

The basic properties of certain fuels using kerosene as the combustible are shown in Table 188 [1] and Fig. 247 [2]. Figure 248 shows the design characteristics of ZhRD using gasoline and liquid oxygen [9].

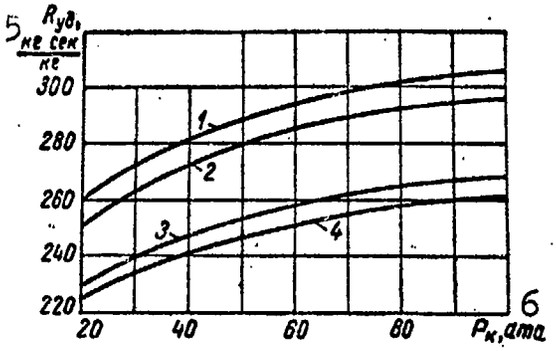



Fig. 247. Theoretical specific thrust $R_{ud}$ of ZhRD as a function of combustion-chamber pressure $P_k$, kerosene burnt with various oxidizers (pressure of gases in exit section of nozzle 1 atm; excess-oxidizer factor $\alpha = 0.8$). 1) Kerosene + liquid oxygen; 2) ethyl alcohol + liquid oxygen; 3) kerosene + (60% $HNO_3$ + 40% $N_2O_4$); 4) kerosene + nitric acid; 5) $R_{ud}$, kg sec/kg; 6) $P_k$ atm abs.

ALCOHOL-BASE COMBUSTIBLES

Alcohols are widely used as a combustible for ZhRD in conjunction with such oxidizers as liquid oxygen and hydrogen peroxide. These alcohols ignite easily with such oxidizers and burn smoothly. The ignition lag is less for alcohols than for hydrocarbons.

The first ZhRD created in the USSR for research purposes, as well as the first German military rocket using ZhRD operated on alcohol and liquid oxygen [7, 14 - 16]. At the present time, alcohols

TABLE 188

Fuels for ZhRD Using Kerosene as the Combustible

| 1 Окислитель | 2 Горючее | 3 Теоретически необходимое количество окислителя, кг окислителя/кг горючего | 4 Теплота сгорания, ккал/кг | 5 Плотность топлива, кг/л при α=1 | 6 Температура горения, °К | 7 Кажущийся мол. вес продуктов сгорания | 8 Удельная тяга: 9 на сек/кг | 8 Удельная тяга: 10 на сек/л |
|---|---|---|---|---|---|---|---|---|
| 11 Азотная кислота (98%-ной концентрации) | 16 Керосин ..... | 5.5 | 1460 | 1.36 | 2950—3000 | 26—27 | 225—235 | 306—315 |
| 12 Четырехокись азота | " ..... | 4.0 | 1550 | 1.38 | 3200 | 25—26 | 235—245 | 325—340 |
| 13 Тетранитрометан | 17 ..... | 6.0 | 1500 | 1.47 | 3200—3360 | 26—27 | 240—250 | 355—370 |
| 14 Жидкий кислород | Этиловый спирт 99,5%-ной концентрации ..... | 1.37 | 2200 | 1.00 | 3550—3650 | 23—25 | 270—280 | 270—280 |
| То же 15 | | 1.95 | 3020 | 0.89 | 3250—3350 | 23—24 | 250—260 | 250—260 |

Note: The specific thrust, combustion temperature, and apparent molecular weight of the gases is determined by calculation for a pressure differential of 50:1 and α in the region that is optimum for the given fuel. The total heat content for kerosenes is assumed to equal 440 kcal/kg.

11) Oxidizer; 2) combustible; 3) theoretically required amount of oxidizer, kg oxidizer/kg combustible; 4) heat of combustion, kcal/kg; 5) fuel density, kg/liter at α = 1; 6) combustion temperature, °K; 7) apparent molecular weight of combustion products; 8) specific thrust; 9) kg sec/kg; 10) kg sec/liter; 11) nitric acid (98% concentration); 12) nitrogen tetroxide; 13) tetranitro- [Key continued on next page.

[Continuation of Key to Table 188] methane; 14) liquid oxygen; 15) the same; 16) kerosene; 17) ethyl alcohol, 93.5% concentration.

TABLE 189

Physical-Chemical Properties of Certain Alcohols as Compared with Kerosene

| 1 Спирт | 2 Формула | 3 Молекулярный вес | 4 Температура кипения, °С | 5 Температура плавления, °С | 6 Теплоемкость (при 20–25°), ккал/кг град | 7 Скрытая теплота испарения, ккал/кг | 8 Плотность $\rho_4^{20}$ | 9 Теплота сгорания, ккал/кг |
|---|---|---|---|---|---|---|---|---|
| 10 Метиловый | $CH_3OH$ | 32.03 | 64.6 | —94.9 | 0.60 | 263 | 0.7813 | 1770 |
| 11 Этиловый | $C_2H_5OH$ | 46.05 | 78.3 | —117.0 | 0.58 | 214 | 0.789 | 2020 |
| 12 Пропиловый | $C_3H_7OH$ | 60.06 | 97.8 | —127.0 | 0.59 | 159 | 0.810 | 2210 |
| 13 Изопропиловый | $C_3H_7OH$ | 60.06 | 82.3 | —88.5 | 0.59 | 160 | 0.781 | 2070 |
| 14 Бутиловый | $C_4H_9OH$ | 74.08 | 117.7 | —89.8 | 0.50 | 143 | 0.817 | 2210 |
| 15 Амиловый | $C_5H_{11}OH$ | 88.10 | 137.9 | —78.5 | 0.50 | 120 | 0.804 | 2220 |
| 16 Гексиловый | $C_6H_{13}OH$ | 102.11 | 155.8 | —51.6 | — | — | 0.819 | 2230 |
| 17 Гептиловый | $C_7H_{15}OH$ | 116.13 | 175.8 | —36.2 | — | — | 0.817 | 2250 |
| 18 Октиловый | $C_8H_{17}OH$ | 130.14 | 194.0 | 21 —14.0 | — | — | 0.827 | 2260 |
| 19 Керосин | $C_{10,7}H_{20}$ | 150.00 20 (Средний) | 150—315 | Ниже —50 | 0.45 | 51 | 0.79 | 3275 |

1) Alcohol; 2) formula; 3) molecular weight; 4) boiling point, °C; 5) melting point °C; 6) heat capacity (at 20 – 25°), kcal/kg degree; 7) latent heat of vaporization, kcal/kg; 8) density, $\rho_4^{20}$; 9) heat of combustion, kcal/kg; 10) methyl; 11) ethyl; 12) propyl; 13) isopropyl; 14) butyl; 15) amyl; 16) hexyl; 17) heptyl; 18) octyl; 19) kerosene; 20) average; 21) below.

are used as combustibles in many countries for various rocket-powered flying craft.

The presence of oxygen atoms in the alcohol molecule can be considered to be partial combustion of the combustible elements in these compounds. Thus the heat of combustion is lower for alcohols than for hydrocarbons. As a result, lower temperature is produced when alcohols are burnt, and this simplifies the design of reliably operating engines. In addition, alcohols have a greater heat capacity and latent heat of vaporization than do petroleum products (Table 189). This fact, as well as the high relative percentage of alcohol contained in the final fuel mixtures (up to 40 – 50%), make it possible to use alcohols successfully to cool the motor-chamber walls. The quite large proportion of the fuel mixture formed by alcohols improves conditions for mixing of the alcohol and oxidizer in the combustion chamber, and provides a high degree of combustion efficiency.

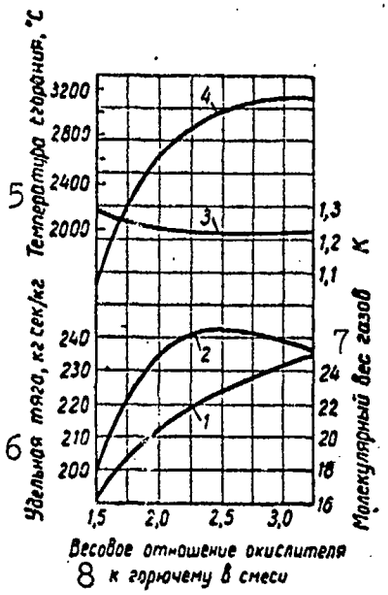



Fig. 248. Design characteristics of ZhRD using gasoline and liquid oxygen. $p_1$ = 21 kg/cm$^2$; $p_1/p_2$ = 20.4; 1) Molecular weight; 2) specific thrust; 3) $K = C_p/C_v$; 4) temperature; 5) combustion temperature, °C; 6) specific thrust, kg sec/kg; 7) molecular weight of gases; 8) weight ratio of oxidizer to combustible in mixture.

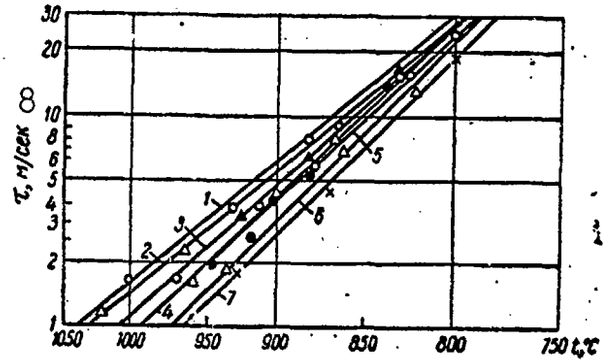



Fig. 249. Variation in ignition lag of alcohols mixed with air as a function of temperature. Alcohols: 1) methyl; 2) ethyl; 3) n-propyl; 4) n-butyl; 5) n-amyl; 6) n-hexyl; 7) n-decyl; 8) τ, m/sec.

The lower combustion temperature of alcohols causes a lower loss of heat owing to dissociation of combustion products than is the case for hydrocarbons; thus in the last analysis alcohols are in no way inferior to hydrocarbons in efficiency.

The various alcohols of normal structure differ relatively little with respect to the ignition lag [17]. A decrease in ignition lag with increasing alcohol molecular weight can be noted (Fig. 249).

The higher alcohols have greater density and a higher boiling point than the lower alcohols (Table 189); the lower monobasic alcohols – methyl and ethyl alcohols and their mixtures – find the greatest practical application as combustibles, however, since they are the cheapest and are supplied by the broadest industrial base.

The relatively high boiling points and low freezing points of alcohols make it possible to use them over a wide range of operating temperatures. Alcohols, as in the case of hydrocarbons, are characterized by negligible corrosive activity with respect to metals. Thus, tanks and fuel apparatus of an engine are made from common readily available and inexpensive materials. The good operating qualities, relatively low combustion temperature, high combustion stability, and good cooling ability were responsible for the choice of alcohols as combustibles in the early period of development of ZhRD. Owing to the fact that alcohols dissolvewell in water, it is possible to use aqueous solutions of alcohols in various concentrations as combustibles.

TABLE 190

Characteristics of Fuels Based on Ethyl Alcohol and Liquid Oxygen [18]

| 1 Концентрация спирта, % | 2 Состав топлива, % | | 5 Теплота сгорания, ккал/кг | 6 Характеристика охлаждающих свойств* |
|---|---|---|---|---|
| | 3 кислород | 4 спирт | | |
| 100 | 67,60 | 32,40 | 2020 | 1,9 |
| 90 | 65,11 | 34,89 | 1935 | 2,2 |
| 80 | 62,53 | 37,47 | 1822 | 2,4 |
| 70 | 59,40 | 40,60 | 1703 | 2,8 |
| 7 Толуол | 75,80 | 24,20 | 2280 | 1,0 |

*The relative amounts of heat required to heat the combustible from 20° to the boiling point with complete vaporization.

1) Alcohol concentration, %; 2) fuel composition, %; 3) oxygen; 4) alcohol; 5) heat of combustion kcal/kg; 6) cooling characteristics*; 7) toluene.

The dilution of alcohols with water on the one hand decreases the heat of combustion (Fig. 250) and the fuel combustion temperature, and on the other hand raises the heat capacity and thermal conductivity; there is consequently an improvement of the cooling ability of the combustible (Table 190).

In the ZhRD for the German V-2 rocket, a 75% aqueous solution

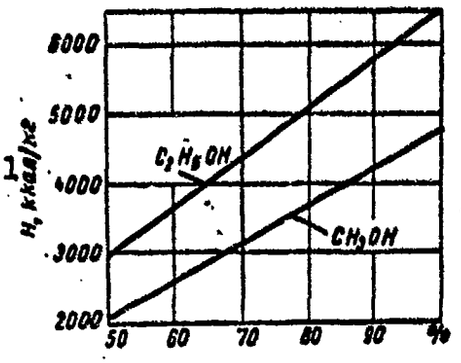



Fig. 250. Heat of combustion of ethyl and methyl alcohol as a function of concentration. 1) N, kcal/kg.

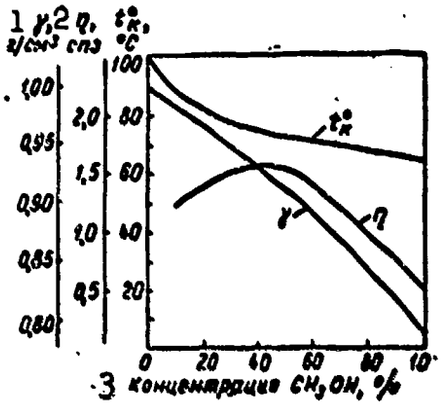



Fig. 251. Physical properties of methyl alcohol. γ) Specific gravity; η) viscosity; $t_к$°) boiling point; 1) γ, g/cm³; 2) η, centipoises; 3) concentration.

of ethyl alcohol was used as the combustible.

Alcohols are not hypergolic in combination with liquid oxygen or hydrogen peroxide. A special igniter is needed to start a motor using an alcohol combustible. Alcohols find almost no application in combinations using nitric acid oxidizers.

Despite their relatively low heat of combustion, alcohols have so far not lost their importance as rocket combustibles, owing to other positive properties and advantages (they are used in the ZhRD in the United States Redstone and Viking rockets, and others); alcohols will clearly not be widely used in the future, since the use of hydrocarbon combustibles has been mastered successfully.

Methyl Alcohol (Wood Alcohol, Methanol, Carbinol)

Methyl alcohol is a colorless transparent low-viscosity liquid with a characteristic alcohol odor resembling the odor of ethyl alcohol.

Figure 251 shows some physical properties of methyl alcohol.

Methyl alcohol burns with a bright-blue sootless flame. Vapors of methyl alcohol form a mixture with air that is easily ignited by a spark.

Methyl alcohol is obtained by dry distillation of wood, or synthetically. This latter process is based upon the reduction of carbon monoxide by hydrogen at a temperature of 200 – 300° and a pressure of 150 – 600 atm in the presence of zinc oxide or other catalysts.

Methyl alcohol is widely used in various branches of technology. It is not a complicated substance to produce, and thus it is a readily available combustible.

Methyl alcohol, which is inferior to ethyl alcohol with respect to energy characteristics, is employed as a combustible in low-power ZhRD (for example in the English Sea Slug guided antiaircraft missile), and also as a substitute for ethyl alcohol. It can also be used in a mixture with ethyl alcohol.

Methyl alcohol has a strong effect on the nervous and vascular systems. Its poisonous characteristics appear most sharply when taken internally, but toxic effects can also appear when the vapors are breathed, or when the liquid alcohol or its vapors act on the skin. When taken internally in small doses, methyl alcohol damages the optic nerve, leading to total blindness, while in large doses it causes death.

In working with methyl alcohol it is necessary to observe precautionary measures.

Ethyl Alcohol (Spirit of Wine, Ethanol)

Ethyl alcohol resembles methyl alcohol in appearance and odor. The boiling point of pure ethyl alcohol is 78.3° and its density at 20° is 0.7893.

The variation in the physical properties of ethyl alcohol with temperature changes is shown in Fig. 252.

Ethyl alcohol has a large volume coefficient of expansion, equal to 0.001 at 20°; it thus changes its volume and density sharply with

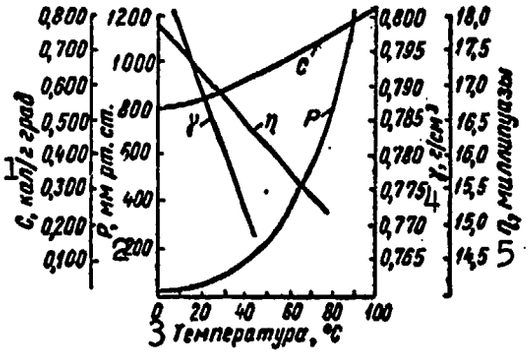



Fig. 252. Physical properties of pure ethyl alcohol at various temperatures (atmospheric pressure). γ) Specific gravity; η) viscosity; C) heat capacity; P) vapor pressure; 1) C, cal/g degree; 2) P, mm Hg; 3) temperature, °C; 4) γ, g/cm$^3$; 5) η, millipoises.

a variation in temperature.

Ethyl alcohol is hygroscopic. The hygroscopicity of the alcohol rises with temperature and with relative humidity. Ethyl alcohol mixes with water in any proportions.

When the alcohol is mixed with water there is a decrease in the mixture volume owing to hydration (formation of hydrates $C_2H_5OH \cdot nH_2O$). The decrease in volume depends upon the proportions in which the alcohol and

TABLE 191

Decrease in Total Volume of Ethyl Alcohol and Water when Mixed (Temperature of 20°)

| 1 Взято для смешивания | | Уменьшение суммарного объема при смешивании, 4 л | 1 Взято для смешивания | | Уменьшение суммарного объема при смешивании, 4 л |
|---|---|---|---|---|---|
| безводного спирта, 2 л | воды, 3 л | | безводного спирта, 2 л | воды, 3 л | |
| 0 | 100 | 0,000 | 60 | 40 | 3,697 |
| 10 | 90 | 0,794 | 70 | 30 | 3,360 |
| 20 | 80 | 1,719 | 80 | 20 | 2,830 |
| 30 | 70 | 2,694 | 90 | 10 | 1,912 |
| 40 | 60 | 3,347 | 100 | 0 | 0,000 |
| 50 | 50 | 3,650 | | | |

1) Taken for mixing; 2) absolute alcohol, liters; 3) water, liters; 4) decrease in total volume upon mixing, liters.

water are mixed, and is characterized by the data shown in Table 191.

The volume drops most when 60 parts of alcohol by volume is mixed with 40 parts of water by volume. If mixing occurs at 20°, we obtain only 96.313 parts by volume of mixture in place of the 100 parts by volume of alcohol and water.

Ethyl alcohol has a very low freezing point: −114°. When the al-

TABLE 192

Freezing Points of Aqueous Solutions of Alcohol

| 1 Содержание спирта, % вес. | 2 Температура замерзания, °C | 1 Содержание спирта, % вес. | 2 Температура замерзания, °C | 1 Содержание спирта, % вес. | 2 Температура замерзания, °C |
|---|---|---|---|---|---|
| 5,1 | —2,1 | 33,3 | —24,2 | 66,1 | —48,0 |
| 9,3 | —4,1 | 37,6 | —28,2 | 70,2 | —56,0 |
| 14,2 | —6,7 | 43,0 | —33,0 | 74,7 | —67,0 |
| 17,8 | —10,2 | 46,7 | —35,4 | 100,0 | —114,0 |
| | | 51,9 | —38,0 | | |
| 24,4 | —15,2 | 56,3 | —42,0 | | |
| 29,0 | —19,1 | 61,4 | —45,0 | | |

1) Alcohol content, % by weight; 2) freezing point, °C.

cohol is diluted with water, the freezing point of the alcohol solutions rises (Table 192).

Ethyl alcohol is easly ignited and burns with a blue dim flame. The vapors of the alcohol form explosive mixtures with air over a broad range of concentrations. The selfignition temperature of the alcohol in air is 510°.

Ethyl alcohol is obtained industrially by the alcohol fermentation of substances containing hydrocarbons (grain, potatoes, beets, etc). The synthetic production of ethyl alcohol has expanded quickly in recent years. The raw materials used to produce synthetic ethyl alcohol are petroleum-refinery gases containing ethylene, sawmill wastes (sawdust, chips, etc.), and cellulose-industry wastes (sulfite alkalis).

There are two methods by which ethyl alcohol can be obtained from petroleum gases:

hydration of ethylene by water vapor at high pressures and temperatures in the presence of a catalyst based upon phosphoric acid:

$$C_2H_4 + H_2O \rightleftarrows C_2H_5OH;$$

reaction of ethylene with concentrated sulfuric acid with the formation of ethyl sulfate.

$$C_2H_4+HOSO_2OH \rightleftarrows C_2H_5OSO_2OH$$

and subsequent hydration of the ethyl sulfate by water

$$C_2H_5OSO_2OH+H_2O \rightleftarrows C_2H_5OH+H_2SO_4.$$

Ethyl alcohol is obtained from wood by hydrolysis of the wood at high temperature in the presence of a catalyst (mineral acid). Here polysaccharides of the wood are converted to very simple sugars, which are then fermented into the alcohol.

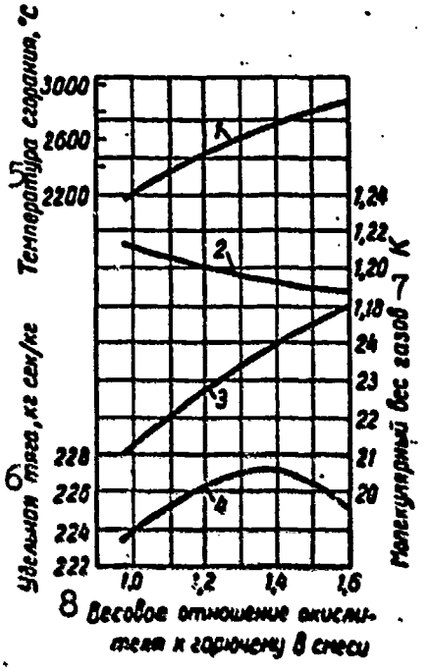



Fig. 253. Design characteristics of ZhRD using liquid oxygen and 75% ethyl alcohol. $p_1$ = 14 kg/cm$^2$; $p_1/p_2$ = 13.6. 1) Temperature; 2) $K = C_p/C_v$; 3) molecular weight; 4) specific thrust; 5) combustion temperature °C; 6) specific thrust, kg sec/kg; 7) molecular weight of gases; 8) weight proportion of oxidizer to combustible in mixture.

The unrefined raw alcohol contains a large quantity of various impurities that impart an unpleasant odor to it, are responsible for metal corrosion, and also have a harmful effect upon the human organism. Thus, the raw alcohol cannot be used as a combustible. Refined ethyl alcohol is used for this purpose. It is obtained by fractional distillation (rectification) of the raw alcohol; during this process, the harmful impurities are removed, and the content of absolute alcohol in the product is increased.

Both pure ethyl alcohol, rectified with a strength of 92 – 94% by weight, and its aqueous solutions are used as rocket combustibles. The addition of water to the alcohol, as we have already noted, decreases the combustion temperature and simultaneously

improves the cooling properties of the combustible. Aqueous solutions of ethyl alcohol are characterized by increased corrosion activity with respect to metals, especially the low-carbon steels. Various corrosion inhibitors are added in order to prevent corrosion.

Figure 253 shows design characteristics for ZhRD using ethyl alcohol and liquid oxygen [9].

Ethyl alcohol is stored in clean steel tanks, drums, and containers. With proper storage, its properties are unchanged over a very long time span.

Ethyl alcohol cannot be stored in a galvanized container, since it reacts with the zinc coating. In this case, a large quantity of amorphous precipitate flakes of white color are formed in the alcohol (zincates). The alcohol becomes cloudy and is unsuitable for use.

When stored for extended periods of time in tanks, the alcohol may separate into layers: the upper layers will contain stronger alcohol and the lower layers weaker alcohol. The difference in the strength of the alcohol in the lower and upper layers of the tank will increase with the strength of the alcohol.

In the practical utilization of alcohol-base combustibles, it is very important to be able to distinguish ethyl alcohol from methyl alcohol. There exist two simple qualitative reactions that may be used to distinguish these two alcohols rapidly.

1. When the alcohols are reacted with vanillin ($C_8H_8O_3$) in the presence of sulfuric acid, compounds are formed that give different colors to the solution.

The reaction is performed as follows.

To 1 ml of the alcohol being tested, we add some crystals of vanillin, and carefully pour 2 ml of concentrated sulfuric acid (specific gravity 1.84) down the wall of the test tube. With vanillin

and sulfuric acid, ethyl alcohol forms a compound that colors the solution a gold-yellow that turns green when allowed to stand for some length of time. With methyl alcohol, the solution acquires a thick rose-colored layer which gradually turns red when allowed to stand. The alcohol has a green hue in a thin layer.

It is possible to use for this reaction ordinary crystalline vanillin of the sort used for household purposes.

2. When iodine reacts with ethyl alcohol in alkali solutions, iodoform is formed as yellow crystals which have a characteristic odor. This forms the basis for a qualitative reaction for ethyl alcohol that may be used to find whether the alcohol concentration in a solution is at least 0.05%. The equation for the chemical reaction taking place can be represented as follows:

$$C_2H_5OH+4J_2+6NaOH \Rightarrow \underset{\downarrow}{CHJ_3}+HCOONa+5H_2O+5NaJ.$$

The qualitative reaction for ethyl alcohol is performed as follows.

Several crystals of iodine are dissolvedin 1 – 2 ml of the alcohol being tested until a dark brown color is obtained. Next a weak solution of sodium hydroxide is obtained until the color vanishes, the solution is heated slightly and allowed to stand. If ethyl alcohol is present, the characteristic yellow crystalline precipitate of iodoform will appear immediately or after the solution has stood for a short time.

No precipitate forms in the presence of methyl alcohol.

An aqueous solution of iodine may be employed in place of crystalline iodine for the reaction.

AMINE-BASE COMBUSTIBLES

In the design of ZhRD, a great deal of attention is paid to pro-

viding reliable engine starting. Ill-timed supply of combustible or oxidizer to the combustion chamber, or a great ignition lag can lead to an explosion and destruction of the engine. The problem of designing a reliably operating engine is successfully solved if a combustible that forms a hypergolic mixture with a given oxidizer is used, and the resulting mixture has a short ignition lag.

An advantage of hypergolic fuels also lies in the fact that their use simplifies the engine starting system, since in this case there is no need for a special device for ignition. In the working regime, such fuels burn more stably, with fewer pulsations and vibrations than forced-ignition fuels. A drawback to hypergolic fuels is the great fire hazard that they present.

The basic quantity characterizing the quality of hypergolic fuels is the ignition lag $\tau$. For safe starting of a motor, $\tau$ should be as small as possible, and in any case should not exceed 0.03 sec [2].

A large number of formulas for combustibles that form hypergolic mixtures with nitric acid have been created on the bases of the amino compounds.

The name amino compounds or amines is given to ammonia derivatives in which one or several hydrogen atoms in the molecule have been replaced by hydrocarbon radicals. In their chemical compositions the aliphatic amines are very similar to ammonia. They have the properties of weak bases. Aqueous solutions of the aliphatic series yield an alkali reaction, since the aliphatic amines form bases with water similar to an ammonium hydroxide, for example:

$$CH_3NH_2+H_2O=[CH_3NH_3]OH.$$

The aromatic amines are weaker bases, and their aqueous solutions show almost no alkali reaction.

Amines combine with mineral acids to yield salts that are quite

soluble in water.

The amines are considered to be among the best combustibles for ZhRD. They possess several positive characteristics: low ignition point, high gas evolution, relatively high density, a broad range of concentrations for ignition, a short ignition lag. The good ignitibility and high combustion stability are responsible for the very wide utilization of amines as combustibles for ZhRD, despite their relatively high cost. As a rule, monoamines are used for this purpose.

The first representatives of the monoamines in aliphatic series — methylamines, dimethylamines, and trimethylamines — are gases at the normal temperature of the material. As the chains of hydrocarbon atoms grow longer, there is a regular increase in boiling point of the amines. When we reach the ethylamines, we find that they are liquids at normal temperatures. The amines have a distinctive sharp unpleasant odor and are soluble in water. The higher amines are solids that are odorless water-insoluble substances.

The monoamines of the aromatic series in pure form are high-boiling liquids or solids with a distinctive odor.

As a rule, the amines react very vigorously with nitric acid to liberate a large amount of heat, and in many cases the reaction is accompanied by ignition of the vapor products formed. The intensity of the reaction and the ability of the amines to ignite spontaneously with nitric acid depend both upon the molecular weight and upon the molecular structure of the amines [20 - 21].

The primary unbranched aliphatic amines (up to 5 carbons atoms in the chain) form a hypergolic mixture with nitric acid; the ability to ignite spontaneously increases with increasing chain length in the homologous series of amines.

The replacement of hydrogen in a hydrocarbon chain by a methyl

or ethyl radical in the α position improves the ability of amines to ignite spontaneously. As in the preceding case, the ignition lag drops as we go from isopropylamine to isohexylamine. Amines with a branched hydrocarbon chain containing 7 or more hydrogen atoms do not form hypergolic combinations with nitric acid.

The replacement of the hydrogen in a hydrocarbon chain by a methyl group in the β position decreases the tendency of the amines to spontaneous ignition. The replacement of hydrogen by a hydroxyl, phenyl, or amino radical increases the tendency toward selfignition.

Secondary symmetric aliphatic amines with unbranched chains form a hypergolic combination with nitric acid where up to 10 hydrogen atoms are contained in the molecule. The ignition lag decreases as we go from diethylamine to diamylamine, and is lower in magnitude than the value for the corresponding primary amine.

The effect of secondary-amine structural branching is essentially the same as in the case of the primary amines: replacement of hydrogen by a methyl radical in the α position decreases the ignition lag; substitution in the β position increases the lag.

Of the tertiary aliphatic amines, triethyl-, tripropyl-, and tributylamines form a very hypergolic mixture with nitric acid. Amines possessing a large number of hydrocarbon atoms do not ignite spontaneously with nitric acid.

The tendency of aliphatic monoamines to ignite spontaneously with nitric acid is increased as we go from the primary to the tertiary amines. This is evidently connected with the increase in amine basicity, which is greater for the tertiary amines than for the primary amines.

The ignition lag for the aromatic amines depends upon the position of the side chains in the ring. Of the three toluidines, only

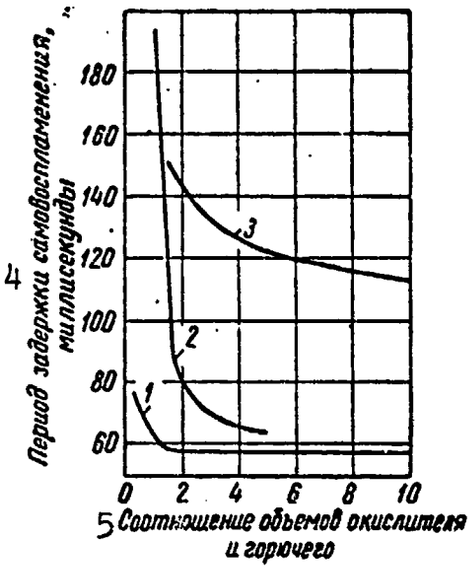



Fig. 254. Effect of volumetric ratio of oxidizer and combustible on ignition lag. 1) Aniline; 2) diethylaniline; 3) methylaniline; 4) ignition lag, milliseconds; 5) volumetric ratio of oxidizer and combustible.

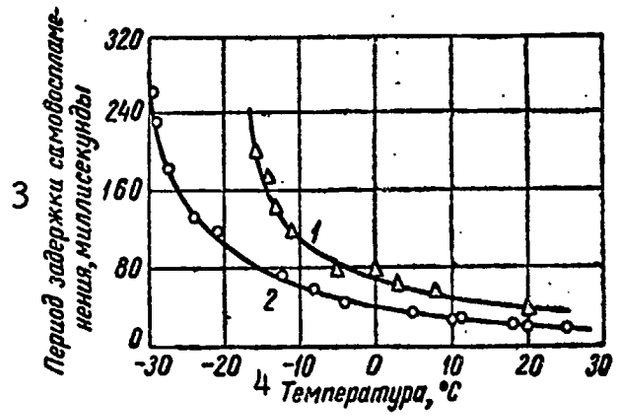



Fig. 255. Ignition lag as a function of temperature. 1) Aniline; 2) furfuryl alcohol (80%) + aniline (20%); 3) ignition lag, milliseconds; 4) temperature, °C.

orthotoluidine ignites spontaneously with nitric acid. The position of the methyl radicals is of great importance for the xylidines: 1, 3, 2- and 1, 3, 4- xylidines have a shorter ignition lag than 1, 2, 3- xylidine.

Mesidine, which has three methyl radicals does not react with nitric acid.

The primary aromatic amines form better hypergolic mixtures with nitric acid than do the secondary or tertiary forms. The concentration of nitric acid has a considerable effect upon the ignition lag, especially for low-activity substances, as does the oxidizer-combustible ratio (Fig. 254).

Where there is a considerable undersupply of oxidizer, ignition is sluggish, and the ignition lag is great. Increasing the quantity of oxidizer to a specified limit facilitates acceleration of the

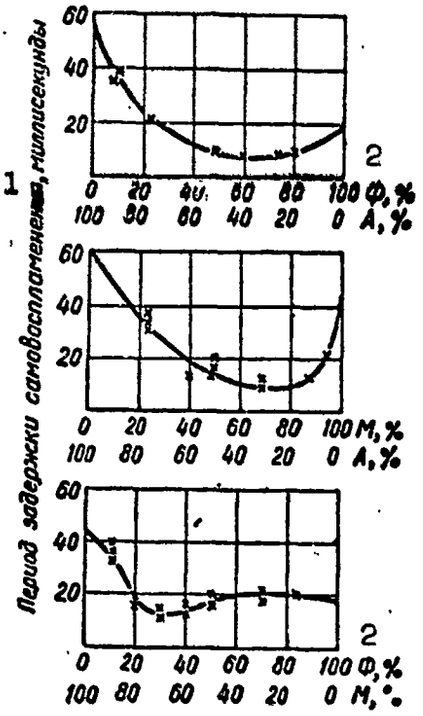



Fig. 256. Ignition lag for combinations of combustibles with concentrated nitric acid as a function of composition. A) Aniline; F) furfuryl alcohol; M) methylpyrrolidine; 1) Ignition lag, milliseconds; 2) F.

reaction; too great an excess of oxidizer leads to an increase in the ignition lag.

A drop in fuel temperature decreases the reaction rate and increases the viscosity of the components, impairing mixing conditions. As a result, an increase in the ignition lag is observed (Fig. 255). The degree of variation in $\tau$ with temperature is not the same for different amines.

The activity of amines in reaction with nitric acid may be increased with the aid of oxidation catalysts; as a rule salts of metals with varying valence (ferric chloride, iron nitrate, salts of high-molecular-weight organic acids) are used for this purpose.

The agents of catalytic activity are the metal cations [16, 19, 22].

The aromatic amines are characterized by high sensitivity to the action of oxidation catalysts. The aliphatic amines are insensitive to this effect.

The ignition lag of amines with nitric acid may be decreased by adding sulfuric acid to the latter. Sulfuric acid, which is a stronger acid than nitric acid, increases the heat of reaction with the amines, and thus ignition occurs more easily.

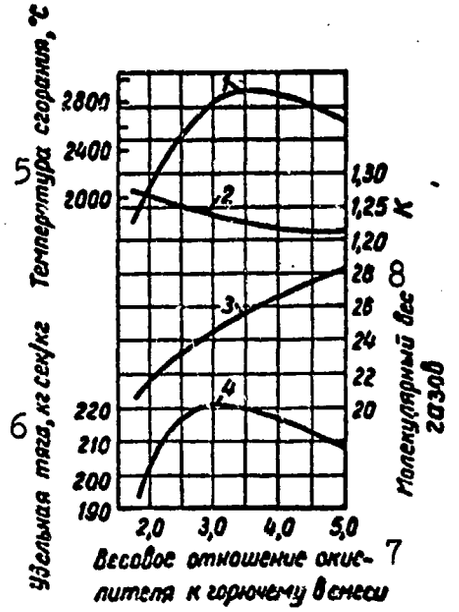



Fig. 257. Design characteristics of ZhRD operating with aniline and fuming red nitric (15% $N_2O_4$). $p_1$ = 21 kg/cm$^2$; $p_1/p_2$ = 20.4; 1) Temperature; 2) $K = C_p/C_v$; 3) molecular weight; 4) specific thrust; 5) combustion temperature, °C; 6) specific thrust, kg sec/kg; 7) weight ratio of oxidizer to combustible in mixture; 8) molecular weight of gases.

Combustible ignition can be improved by the creation of multicomponent systems. Figure 256 shows the way in which the ignition lag of various combustibles with nitric acid depends upon the mixture composition [18]. As the figure shows, the ignition lag of the mixtures varies nonadditively. A specific mixture composition corresponds to a minimum value for $\tau$. Thus, for example, for the mixture containing 40% aniline and 60% furfuryl alcohol, the ignition lag is 0.008 sec, while for the pure products, it is 0.06 and 0.018 sec respectively.

A combustible forming hypergolic mixtures can be employed in ZhRD as a basic type of combustible or as an auxiliary substance, to ignite the mixture when nonhypergolic fuel combinations are used.

Aniline, triethylamine, and xylidine find the widest practical application as combustibles.

Aniline

In the pure form, aniline is a colorless oily easily oxidized liquid that turns dark upon standing, especially in the light. Technical-grade aniline is called aniline oil. The boiling point of aniline is 184.4°, the freezing -6.2°. Aniline has the relatively high density of 1.024 g/cm$^3$ at 20°. It is a poison. As do all aromatic amines,

aniline has the properties of a weak base and yields salts with mineral acids.

Aniline is one of the important products of the aniline dye industry.

At the present time, aniline is obtained from nitrobenzene by reduction of the nitro group to the amino radical in a hydrochloric medium in the presence of a catalyst, and from chlorobenzene by substitution of an amino radical for the chlorine atom.

In conjunction with nitric acid-base oxidizers, aniline is used as a hypergolic combustible in many American rockets (Corporal, Vampire, Aerobee (second stage), Nike (second stage)) [1].

Furfuryl alcohol is sometimes added to aniline in order to lower the freezing point; this also improves ability to ignite spontaneously upon contact with nitric acid, and in almost no way impairs the operating characteristics of the fuel. A mixture of aniline with furfuryl alcohol is used as the starting combustible (specification MPD-229A) for the American Nike-Ajax rocket.

The design characteristics of a ZhRD using aniline and nitric acid, after Satton, are shown in Fig. 257 [9].

Triethylamine

Triethylamine is a transparent mobile light-yellow liquid. Its density at 20° is 0.728, its boiling point 90°. The freezing point of triethylamine is very low (-115°). Triethylamine is very irritating to the central nervous system. It is normally mixed with xylidine when used as a combustible.

Xylidine (Aminoxylol)

Xylidine is a high-boiling oily transparent liquid ranging in color from yellow to light brown; it is lighter than water (its density is 0.978 at 20°). The boiling point of xylidine is very high

(216°), and its freezing point is -54°. It is widely employed in our industry for the production of azo dyes.

The starting product for the production of xylidine is technical xylol, which is a mixture of meta-, ortho-, and paraisomers. Nitration of xylol produces technical nitroxylol, which is a mixture of various isomer products.

Technical nitroxylol is reduced with the aid of iron filings to xylidene in a hydrochloric medium. Technical xylidene is subjected to refining.

When mixed with triethylamine, xylidene may be used as a hypergolic combustible in conjunction with nitric acid-base oxidizers. The most common mixture consists of 50% triethylamine and 50% xylidene. This mixture was employed in many German ZhRD during the Second World War under the name Tonka-250. It has a very nearly optimum composition that provides a minimum ignition lag. Certain physical constants for Tonka-250 combustible at various temperatures and design data for the specific thrust ZhRD are shown in Figs. 258 and 259.

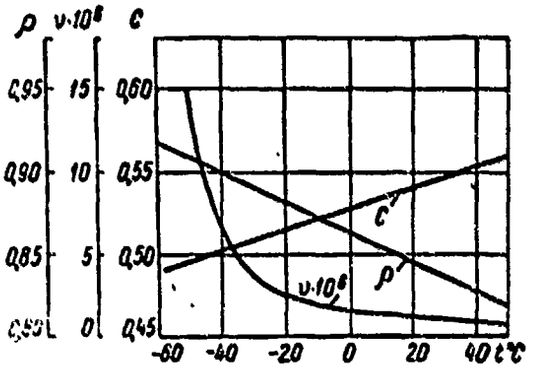



Fig. 258. Physical properties of Tonka-250 combustible as a function of temperature (abnormal pressure); ρ) density in kg/liter; C) heat capacity in kcal/kg °C; ν) kinematic viscosity in m²/sec.

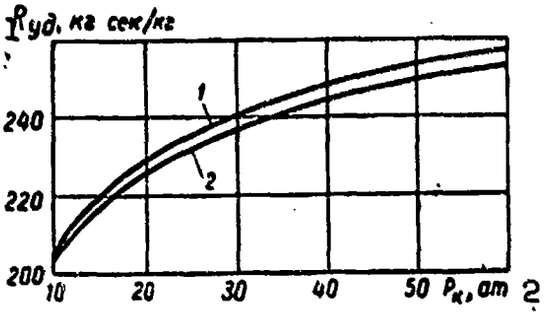



Fig. 259. Theoretical specific thrust of ZhRD ($R_{ud}$) as a function of combustion-chamber pressure ($P_k$); 1) Tonka-250 + (80% $HNO_3$ + 20% $N_2O_4$); 2) kerosene + + (80% $HNO_3$ + 20% $N_2O_4$) [62]; (pressure of gases in output section of 1 atm, excess-oxidizer factor α = 0.8); 1) $R_{ud}$, kg sec/kg; 2) $P_k$, atm.

A general drawback to amine-base combustibles is their relatively high cost and scarcity.

In order to increase the resources for hypergolic combustibles, they are sometimes mixed with petroleum products or other nonhypergolic combustibles [18]. When mixed with an oxidizer, the hypergolic component is an ignition initiator.

In many cases, an amine-base hypergolic combustible is used not as the main combustible, but as an auxiliary fuel to ignite the fuel in chemical-ignition systems.

Ammonia

Liquid ammonia can be used as a combustible for ZhRD. Its heat of combustion with liquid oxygen (1640 kcal/kg) is lower, for example, then that of hydrocarbon combustibles. But when it is burnt with oxygen, almost the same specific thrust is obtained as when kerosene is burnt with oxygen. The combustion temperature of ammonia is slightly lower than that obtained upon combustion of hydrocarbon combustibles.

Liquid ammonia with liquid fluorine as the oxidizer is a very good combination. Such a fuel makes it possible to obtain high specific engine thrust (340 – 350 kg sec/kg). The gain in efficiency when ammonia is used as a combustible is associated with the better thermodynamic properties of the combustion products of the fuel (low molecular weight, considerable content of diatomic gas).

Under normal conditions, ammonia is a colorless easily liquefied gas with the characteristic sharp odor of "ammonia water." At a pressure of 6 – 7 atm at normal temperatures, ammonia goes into the liquid phase.

The boiling point of ammonia is 33.4°, the freezing point -77.7°, the density at the boiling point 0.68 g/cm$^3$. The viscosity of liquid ammonia is considerably less than the viscosity of water.

The availability and cheapness of ammonia facilitates its use in ZhRD. It is an extremely important product of the chemical industry, and is produced in very large quantities.

Ammonia is obtained commercially by synthesis from the nitrogen of the air and hydrogen. The synthesis is carried out at high temperatures (400 – 500°) and pressures (100 – 1000 atm) in the presence of a catalyst.

Under normal conditions, ammonia is quite stable. It burns with a yellow flame in an oxygen atmosphere when a flame is applied.

The alkaline properties of ammonia cause it to corrode nonferrous metals.

A substantial drawback to ammonia, complicating its utilization is the low boiling point.

Ammonia is toxic, and damages the mucous membranes of the eye and the respiratory tracts.

Basic data on certain fuels using ammonia and amines as combustibles are given in Table 193 [1].

HYDRAZINE AND ITS DERIVATIVES

Hydrazine and its derivatives, hydrazine hydrate, dimethylhydrazine, etc. occupy an important place among the nitrogen-containing compounds that are employed as combustibles for ZhRD.

Hydrazine ($N_2H_4$)

Hydrazine is a product of the partial oxidation of ammonia, and forms when ammonia reacts with sodium hypochlorite:

$$2NH_3+NaOCl=H_2O+N_2H_4+NaCl.$$

The structural formula of hydrazine is $H_2N - NH_2$.

Hydrazine is a colorless strongly hygroscopic quite viscous liquid that fumes in air. The boiling point of pure hydrazine is 113.5°, the freezing point about 2°, and the density at 20° is

TABLE 193

Data for Comparison of ZhRD Fuels Employing Amines and Ammonia as Combustibles

| 1 Окислитель | 2 Горючее | 3 Теоретически необходимое количество окислителя, кг окислителя/кг горючего | 4 Теплота сгорания, ккал/кг | 5 Плотность топлива, кг/л при α = 1 | 6 Температура горения, °К | 7 Кажущийся молекулярный вес продуктов сгорания | 8 Удельная тяга: 9 кг сек/кг | 8 Удельная тяга: 10 кг сек/л |
|---|---|---|---|---|---|---|---|---|
| 11 Азотная кислота 98%-ной концентрации | 16 50% триэтиламина и 50% ксилидина | 4,6 | 1490 | 1,32 | 3000 | 26—27 | 230—240 | 305—310 |
| 12 То же | 17 80% анилина и 20% фурфурилового спирта . . . . . | 3,9 | 1420 | 1,39 | 3050 | 26—27 | 210—230 | 295—315 |
| 13 Жидкий кислород | 18 Диэтиламин . . . . . | 2,97 | 2230 | 0,99 | 3550—3650 | 26—28 | 270—280 | 270—280 |
| 12 То же | 19 Аммиак . . . . . | 1,41 | 1650 | 0,89 | 3000—3050 | 19—20 | 280—290 | 250—258 |
| 14 Жидкий фтор | » . . . . . | 3,36 | 2315 | 1,18 | 4500—4600 | 20—21 | 340—350 | 400—415 |
| 15 Жидкий кислород | 20 Керосин . . . . . | 3,37 | 2200 | 1,00 | 3550—3650 | 23—25 | 270—280 | 270—280 |

Note: The specific thrust, combustion temperature, and apparent molecular weight of gases are determined by calculation for a pressure differential of 50:1 and α in the region optimum for the given fuel.

1) Oxidizer; 2) combustible; 3) theoretically required quantity of oxidizer, kg, oxidizer/kg combustible; 4) heat of combustion, kcal/kg; 5) fuel density, kg/liter at α = 1; 6) temperature of combustion, °K; 7) apparent molecular weight of combustion products; 8) specific thrust; 9) kg sec/kg; 10) kg sec/liter; 11) nitric acid, 98% concentration; 12) the same; 13) liquid oxygen; 14) liquid fluorine; 15) liquid oxygen; 16) 50% triethylamine and 50% xylidine; 17) 80% aniline and 20% furfuryl alcohol; 18) diethylamine; 19) ammonia; 20) kerosene.

1.01 g/cm$^3$.

Hydrazine dissolves well in water, alcohols, amines, and other polar solvents. In nonpolar solvents such as hydrocarbons, halogenated hydrocarbons, etc., they will not dissolve.

As it is a strong reducing agent, hydrazine easily reacts with many substances, and especially with oxidizers.

Free hydrazine is able to combine with a molecule of water to

form hydrazine hydrate $N_2H_4 \cdot 2H_2O$. This compound is a colorless liquid with a boiling point of 118°, a freezing point of -52°, and a density at 20° of 1.03 g/cm$^3$.

In contact with the oxygen of the air, hydrazine ignites and burns with a violet flame. When heated to a temperature of about 350°, it breaks down quietly into $N_2$ and $NH_3$ [23]. At higher temperatures, it tends to explosive decomposition [24]. Owing to this property of hydrazine, it cannot be used to cool a motor combustion chamber.

The decomposition of hydrazine is accelerated in the presence of oxides of iron, chromium, copper, and other catalysts [25]. This reaction, which is accompanied by the evolution of heat and gaseous products, makes it possible to use hydrazine as a monopropellant.

Hydrazine has a relatively low heat of combustion (1940 kcal/kg with oxygen, 2430 kcal/kg with fluorine), but a small quantity of oxidizer is needed for its combustion. It is characterized by high gas evolution.

The temperature of combustion of hydrazine is relatively low; in this connection the loss of heat owing to dissociation of its combustion products is not large.

The excellent thermodynamic properties of hydrazine when it is burnt with all known oxidizers make it possible to obtain high specific thrust from an engine (Fig. 260). With oxidizers based on nitric acid, fluorine, and concentrated hydrogen peroxide, it ignites spontaneously with a short ignition lag. Hydrazine was employed with hydrogen peroxide by the Germans during the Second World War for the Me-163 fighter-interceptor with ZhRD, and a mixture with methyl alcohol in the Val'ter rocket engine [16].

The utilization of hydrazine as a combustible involves certain difficulties in connection with its high freezing point and the need

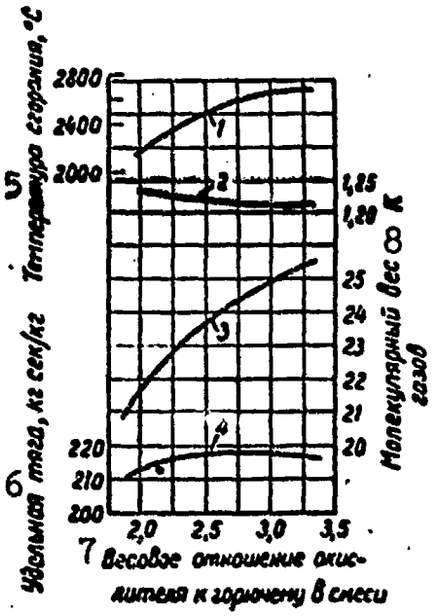



Fig. 260. Design characteristics of ZhRD using hydrazine and liquid oxygen [9]. $p_1$ = 20.8 kg/cm$^2$; $p_1/p_2$ = = 20; 1) Temperature; 2) $K = C_p/C_v$; 3) molecular weight; 4) specific thrust; 5) combustion temperature °C; 6) specific thrust, kg sec/kg; 7) weight ratio of oxidizer to combustible in mixture; 8) molecular weight of gases.

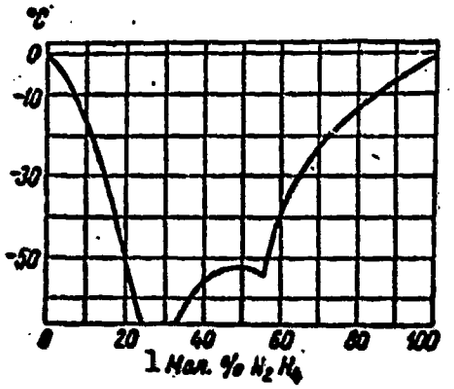



Fig. 261. Curve for crystallization of hydrazine-water mixture [28]. 1) Mol % $N_2H_4$.

to insulate it completely against air during storage. As yet, no effective additives have been found that will lower the freezing point of hydrazine without adversely affecting its energy characteristics.

In many cases, the role of the combustible is played not by hydrazine but by a product of its reaction with water (hydrazine hydrate), which has a very low freezing point (Fig. 261). The energy characteristics of hydrazine hydrate are considerably poorer than those of hydrazine, however.

Pure hydrazine may be used in ZhRD ballistic missiles, provided that launching conditions permit the utilization of a combustible with a high freezing point [26]. According to published information, the ZhRD in the second stage of the Centaur rocket, designed in the United States, will use hydrazine (specification Mil-H-26536) and nitrogen tetroxide [27].

The cost of hydrazine is relatively high.

Hydrazine is very toxic, and ignites easily. As a result, it is necessary to observe precautionary measures in handling this material [28].

Dimethylhydrazine

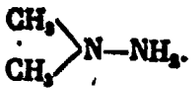
In recent years, information has appeared on the application of unsymmetric dimethylhydrazine* (dimazine) as a combustible for the ZhRD of many rockets; this substance is a hydrazine derivative. Thus, it is used as the combustible in the motors of rockets of the Nike, Rascal [29], Vanguard [25, 30] and Explorer [31] types, and in the booster of the Bomarc rocket interceptor [32]. Combined with liquid oxygen, dimethylhydrazine is used in the first-stage rocket motor that was used in the United States in 1957 to launch an artificial Earth satellite [18, 33]. Owing to the low hydrogen content of the dimethylhydrazine molecule, it is inferior to hydrazine in energy characteristics, but compensates for this in its better operating qualities.

Dimethylhydrazine easily ignites spontaneously with nitric acid-base oxidizers. With liquid oxygen it is ignited from an external ignition source. The ignition lag of dimethylhydrazine with fuming nitric acid (several milliseconds) is the lowest of all presently known fuel compositions [29]. The utilization of dimethylhydrazine as a combustible provides easy starting and operating stability of the engine under various operating conditions [34] and, in addition, makes it possible to increase somewhat the engine thrust characteristics as compared with other nitrogen-containing hypergolic combustibles. The characteristics of fuels for ZhRD using hydrazines as combustibles are shown in Table 194.

In the United States, dimethylhydrazine is produced to the

MIL-D-25604 and MPD-540A specifications.

Dimethylhydrazine is a colorless clear liquid with a sharp unpleasant odor characteristic of the organic amines. The structural formula of unsymmetric dimethylhydrazine is as follows:



Dimethylhydrazine has the chemical nature of an organic base.

The physicochemical constants of pure dimethylhydrazine are as follows [35]:

| | |
|---|---|
| Molecular weight | 60.08 |
| Density at 20° | 0.795 |
| Coefficient of volume expansion at 25° | 0.00133 |
| Boiling point, °C | 63 |
| Freezing point, °C | -57.2 |
| Vapor pressure at 25°, mm Hg | 157 |
| Viscosity at 25°, centipoises | 0.509 |
| Flash point in closed vessel, °C | 1.1 |
| Specific heat capacity at 25°, cal/g-mole degree | 39.2 |
| Heat of combustion, kcal/mole | 473 |
| Thermal conductivity at 25°, cal/sec cm °C | $4.8 \cdot 10^{-4}$ |
| Surface tension at 25°, dyne/cm | 28 |
| Index of refraction at 25° | 1.4058 |
| Heat of combustion (lower-limit) in oxygen, kcal/kg | 2200 |

TABLE 194

Characteristics of ZhRD Fuels Using Hydrazines as Combustibles

| 1 Окислитель | 2 Горючее | 3 Теоретически наиболее важное количество окислителя, кг окислителя/кг горючего | 4 Теплота сгорания, ккал/кг | 5 Плотность топлива, кг/л при α = 1 | 6 Температура горения, °К | 7 Кажущийся мол. вес продуктов сгорания | 8 Удельная тяга | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | 9 на сек/кг | 10 на сек/л |
| 11 Жидкий кислород | 15 Диметилгидразин . . | 2.1 | 2200 | 1.02 | 3300—3400 | 22 | 250—250 | 250—250 |

TABLE 194 (Continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 12 Жидкий фтор | Гидразин 16 . . . . | 2,38 | 2230 | 1,32 | 4600—4700 | 20—21 | 340—350 | 450—455 |
| 13 Перекись водорода 80%-ной концентрации | 17 50% гидразингидрата и 50% метилового спирта . . . . . | 2,72 | 1020 | 1,30 | 2600 | 20—21 | 210—220 | 275—285 |
| 14 Азотная кислота 98%-ной концентрации | 18 50% триэтиламина и 50% ксилидина . . | 4,6 | 1490 | 1,32 | 3000 | 26—27 | 230—240 | 305—370 |

1) Oxidizer; 2) combustible; 3) theoretically required quantity of oxidizer, kg, oxidizer/kg of combustible; 4) heat of combustion, kcal/kg; 5) fuel density, kg/liter at $\alpha = 1$; 6) combustion temperature, °K; 7) apparent molecular weight of combustion products; 8) specific thrusts; 9) kg sec/kg; 10) kg sec/liter; 11) liquid oxygen; 12) liquid fluorine; 13) hydrogen peroxide, 80% concentration; 14) nitric acid, 98% concentration; 15) dimethylhydrazine; 16) hydrazine; 17) 50% hydrazine hydrate and 50% methyl alcohol; 18) 50% triethylamine and 50% xylidine.

The properties of technical grade dimethylhydrazine are as follows [30].

| | |
|---|---|
| Content of pure dimethylhydrazine in % by weight, no less than . . . . . | 98 |
| Density, $\rho_4^{25}$ . . . . . | 0.783-0.786 |
| Boiling range: | |
| 10% evaporates at temperature in °C not below . . . . . | 61.7 |
| 90% evaporates at temperature in °C not above . . . . . | 64.4 |
| Freezing point, °C . . . . . | -56.7 |

The chief advantage of dimethylhydrazine over hydrazine is its relatively low freezing point (-57.2°), which makes it convenient from the operating viewpoint.

Dimethylhydrazine mixes in any proportions with water, petroleum products, alcohol, and many organic solvents. It is oxidized by the oxygen of the air, reacts with carbon dioxide, forming solid salts, and thirstily absorbs moisture from the air. Thus, storage in an unsealed container will lead to rapid deterioration in its quality. In

order to avoid damage to the product, as well as from safety considerations, it is recommended that dimethylhydrazine be stored under a nitrogen blanket.

Containers for storing and transporting dimethylhydrazine are made from ordinary steel. In addition, stainless steel, aluminum and its alloys, nickel, monel, and magnesium can be used as structural materials in contact with dimethylhydrazine. It is not recommended that copper and alloys with a high copper content be used in contact with dimethylhydrazine [36].

Dimethylhydrazine is a good solvent. It causes many well-known lining and packing materials to swell and soften. Teflon, polyethylene, and certain rubbers are resistant to dimethylhydrazine [36]. Dimethylhydrazine has good thermal stability. It breaks down in sealed capillaries only at temperatures of 370-425°.

Dimethylhydrazine is a highly toxic substance. All operations with it should be carried out in gas masks and protective clothing [39].

Dimethylhydrazine forms explosive mixtures with air over a wide range of concentrations – from 2 to 99% (by volume). It ignites easily and thus it is necessary in handling this material to observe strictly all fire safety measures [24].

Dimethylhydrazine is obtained by relatively uncomplicated methods, and the raw materials are plentiful.

It may be obtained from dimethylamine and nitrous acid (Fisher's method) [28].

The p-nitrosodimethylamine is reduced in the presence of zinc in an acetic acid medium:

$$(CH_3)_2NNO + [H] \xrightarrow[CH_3COOH]{Zn} (CH_3)_2NNH_2 + H_2O.$$

Another method of obtaining dimethylhydrazine is the Raschig modification process, developed and perfected for the production of hydrazine [28]. In the first stage, a solution of sodium hypochlorite is treated with ammonia in order to obtain chloramine. Dimethylhydrazine is then obtained from chloramine and dimethylamine according to the diagram

$$NH_3+NaOCl \rightarrow NH_2Cl+NaOH,$$
$$NH_2Cl+(CH_3)_2NH+NaOH \rightarrow (CH_3)_2NNH_2+NaCl+H_2O.$$

After the reaction mass has been dewatered and distilled, pure dimethylhydrazine is obtained.

In recent years, chloramine has been obtained by direct chlorination of ammonia.

At present, dimethylhydrazine is produced in the United States by several companies; a tendency has been noted toward increased production.

In contrast to hydrazine, dimethylhydrazine dissolves well in petroleum products. Up to 40% dimethylhydrazine is added to the American JP-4 petroleum fuel in order to improve combustion stability [26].

It has been reported [26] that dimethylhydrazine mixed with diethylenetriamine (Hydyne combustible) has been used as a combustible.

LIQUID HYDROGEN AS A COMBUSTIBLE

Among the combustibles for ZhRD, liquid hydrogen should be singled out. The high energy characteristics of liquid hydrogen have long been known. The first ideas as to its utilization for combustion in ZhRD with liquid oxygen were advanced by K.E. Tsiolkovskiy [38].

A liquid hydrogen-liquid oxygen mixture ignites easily with a short ignition lag, and has a very high heat of combustion, equal to 3010 kcal/kg. A hydrogen plus oxygen fuel is characterized by high normal flame-propagation rates and wide concentration limits for igni-

tion. At the same time, such a fuel is characterized by large gas evolution (1240 liter/kg). The combustion temperature of hydrogen in oxygen is relatively low (2140°). All of these quantities make liquid hydrogen a very valuable combustible. Its use in a ZhRD permits a considerable increase in engine specific thrust in comparison with other fuels for a lower fuel combustion temperature.

Table 195 gives some characteristics of fuels based on liquid hydrogen [39], and Fig. 262 gives design characteristics for a ZhRD using liquid hydrogen and oxygen [9].

Gaseous hydrogen is the lightest of the gases. Liquid hydrogen is a transparent colorless extremely light and mobile liquid with very

TABLE 195

Some Characteristics of Fuels Based on Hydrogen [39]

| 1 Топливо | 2 Отношение окислителя к горючему | 3 Температура горения, °С | 4 Теоретическая удельная тяга, кг сек/кг | 5 Удельный вес топлива |
|---|---|---|---|---|
| 6 Водород — фтор . . . . | 9,42 | 4466 | 371 | 0,457 |
| 7 Водород — озон . . . . | 3,77 | 2465 | 356 | 0,269 |
| 8 Водород — четырехокись азота . . . . . | 2,65 | 2360 | 373 | 0,230 |
| 9 Водород — кислород . . | 11,5 | 3100 | 279 | 0,565 |
| | 2,65 | 2141 | 345 | 0,970 |

1) Fuel; 2) oxidizer-combustible ratio; 3) combustion temperature, °C; 4) theoretical specific thrust, kg sec/kg; 5) fuel specific gravity; 6) hydrogen-fluorine; 7) hydrogen-ozone; 8) hydrogen-nitrogen tetroxide; 9) hydrogen-oxygen.

low boiling point (-253°) and freezing point (-257°). Liquid hydrogen has very low density, 0.07 g/cm$^3$ (at the boiling point). A hydrogen-air mixture will explode from a spark over a broad range of concentrations – from 5 to 95%.

When stored in vessels open to the atmosphere, hydrogen upon coming into contact with air solidifies and, being heavier, drops to the

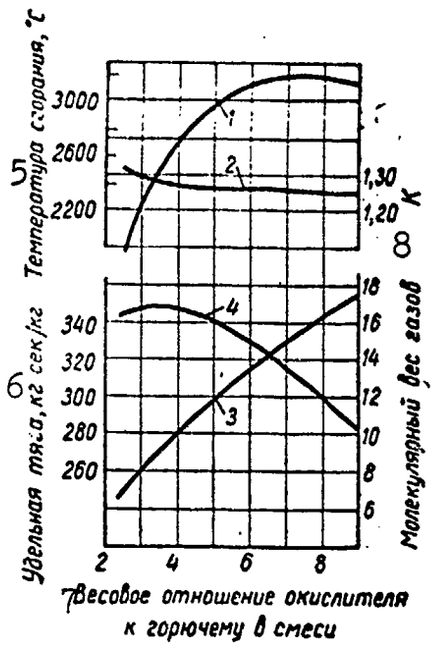



Fig. 262. Design characteristics for ZhRD using liquid hydrogen and oxygen. $p_1$ = 21 kg/cm$^2$; $p_1/p_2$ = 20.4; 1) Temperature; 2) $K = C_p/C_v$; 3) specific thrust; 4) molecular weight; 5) ignition temperature, °C; 6) specific thrust, kg $\frac{\text{sec}}{\text{kg}}$; 7) weight proportion of oxidizer to combustible in mixture; 8) molecular weight of gases.

bottom of the vessel. When this happens, a very dangerous explosive mixture forms.

In this connection, liquid hydrogen must be stored in vessels insulated from the air under high pressure, and even this does not eliminate the explosion hazard [40].

Until recently, liquid hydrogen was obtained by cooling hydrogen compressed to 140 atm with liquid air or nitrogen, and subsequent expansion of the hydrogen [39]. Such a high-pressure system is not justified, however. Today we have available a low-pressure system using circulating gaseous helium that maintains a temperature somewhat below the boiling point of hydrogen at the cold end of the system [39]. As a result, the hydrogen which is at somewhat more than atmos-

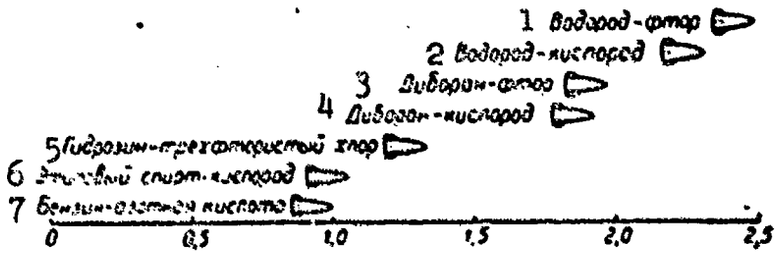



Fig. 263. Relative range of rockets using various fuels [51]. 1) Hydrogen-fluorine; 2) hydrogen-oxygen; 3) diborane-fluorine; 4) diborane-oxygen; 5) hydrazine-chlorine trifluoride; 6) ethyl alcohol-oxygen; 7) gasoline-nitric acid.

pheric pressure is cooled and liquified. Helium installations are sim-

ple to service, easily installed, and may be used under field conditions. The first plant for producing liquid hydrogen was built in the United States in 1957 [8]. At present, liquid hydrogen is produced in large quantities.

Special helium-cooled vessels and tanks have been built in the United States for storing and transporting liquid hydrogen; they provide minimum product losses owing to evaporation. The vessels consist of two shells – an inner shell (of stainless steel) and an outer shell; a high vacuum is set up between them. In the upper portion of the inner shell there are special condensing rings in which gaseous helium is circulated for continuous removal of heat from the hydrogen.

Before liquid hydrogen is charged into appropriate vessels, they are first cooled with liquid nitroger.

The use of liquid hydrogen is complicated by the fact that its density is so low and the complexities involved in storing and handling it. The low density of liquid hydrogen makes it necessary to build very large fuel tanks, which inevitably leads to a considerable increase in rocket size. The very low boiling point of hydrogen greatly complicates storage and the choice of materials for manufacturing tanks and fuel apparatus, since the majority of metals become brittle at low temperetures.

The high energy characteristics of liquid hydrogen make it a very promising combustible, especially for long-range rockets (Fig. 263) [39, 41, 49]. ZhRD working on liquid $H_2$ and $F_2$ have recently been developed [42]. According to published reports, the third-stage motors of the large Saturn and Centaur ballistic missiles under contruction in the USA will use liquid hydrogen and oxygen [43].

A METAL-BASE COMBUSTIBLE

The attempt to increase the specific thrust of ZhRD has led to

unceasing searches for new fuels having increased energy characteristics. Almost all chemical elements in the Mendeleyev periodic system have been investigated.

Table 196 shows the basic properties of fuels consisting of elements having a very large reserve of chemical energy, and the calculated specific thrust obtained when they are burnt in ZhRD [44-46]. The heat of combustion was determined on the basis of the heat of formation of the corresponding oxides (fluorides), and the low heat of combustion, with an allowance for the heat expended in vaporizing the combustion products.

As the table shows, presently feasible fuels for ZhRD made up of the combustible elements hydrogen and carbon and the oxidizing element oxygen have the lowest reserve of chemical energy. Several combustibles such as beryllium, lithium, and other metals have considerably greater (by factors of 2-2.5) heats of combustion in combination with oxygen or fluorine than other types of combustible, and relatively high density (1.73-2.70 g/cm$^3$). Owing to the high density of metals, the specific heat of combustion is extremely large for them. For example, for a beryllium-oxygen fuel combination, it will be 8850 kcal/liter, for magnesium and fluorine, 5550 kcal/liter. In this connection, many authors have suggested that it is possible to increase the specific thrust of ZhRD considerably by using metals as the combustible.

The first ideas of using metal fuels were advanced by G.E. Tsander. Later Yu.V. Kondratyuk and G.E. Langemak performed calculations that demonstrated the possibility of using beryllium, boron, lithium, aluminum, silicon, and certain hydrides of metals and organometallic compounds as combustibles [47, 48].

Metals that are solid at ordinary temperatures may be burnt in an engine in the molten condition or as a powder dispersed in the combus-

tion chamber. The practical application of such methods involves great difficulty, however. It is more convenient to use metals in ZhRD in the form of suspensions or colloidal solutions in which the dispersed substance is a finely divided metal, and the dispersion medium a liquid combustible, or in the form of organometallic compounds dissolved in a combustible.

TABLE 196

Basic Properties of Elementary Fuels

| 1 Горючее | 2 Окислитель | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3 кислород | | | | | | | | 4 фтор | | | | | | | |
| | 5 продукты сгорания | 6 теплота сгорания, ккал/кг | | 7 мол. вес продуктов сгорания | 8 температура кипения продуктов сгорания, °С | 9 плотность, г/см³ | 10 удельная тяга, кг сек/кг | | 5 продукты сгорания | 6 теплота сгорания, ккал/кг | | 7 мол. вес продуктов сгорания | 8 температура кипения продуктов сгорания, °С | 10 удельная тяга, кг сек/кг | |
| | | 11 низшая | 12 высшая | | | | $P/P_0 = 25$ | $P/P_0 = 100$ | | 11 низшая | 12 высшая | | | $P/P_0 = 25$ | $P/P_0 = 100$ |
| 13 Водород | 21 $H_2O$ (газообразные) | — | 3215 | 18,02 | 100 | — | 322 | 370 | 21 HF (газообразные) | 3190 | 3190 | 20,01 | — | 374 | 420 |
| 14 Литий | 22 $Li_2O$ (твердые) | 4760 | 3760 | 29,88 | 1300 | 0,53 | 334 | 378 | 22 LiF (твердые) | 5650 | 3220 | 25,94 | 1960 | 379 | 424 |
| 15 Бериллий | 22 BeO (твердые) | 5400 | 23 Отрицательная | 25,01 | 3900 | 1,85 | — | — | 22 $BeF_2$ (твердые) | 4830 | 4000 | 47,01 | 850 | 358 | — |
| 16 Бор | 22 $B_2O_3$ (твердые) | 4340 | 3300 | 69,94 | — | 2,30 | 251 | 290 | 21 $BF_3$ (газообразные) | 3790 | 3790 | 67,82 | — | 305 | 348 |
| 17 Углерод | 21 $CO_2$ (газообразные) | 2140 | 2140 | 44,01 | −78 | 2,25 | 263 | 300 | 21 $CF_4$ (газообразные) | 1830 | 1830 | 88,01 | — | 187 | 220 |
| 18 Магний | 22 MgO (твердые) | 3630 | 23 Отрицательная | 40,32 | 2250 | 1,74 | — | — | 22 $MgF_2$ (твердые) | 4230 | 2700 | 62,32 | 1110 | 294 | 335 |
| 19 Алюминий | 22 $Al_2O_3$ (твердые) | 3940 | 2680 | 101,94 | 2700 | 2,70 | 227 | 270 | 22 $AlF_3$ (твердые) | 3700 | 3350 | 83,97 | 1110 | 284 | — |
| 20 Кремний | 22 $SiO_2$ (твердые) | 3420 | 2060 | 60,06 | 1900 | 2,40 | 253 | — | 21 $SiF_4$ (газообразные) | 3550 | 350 | 104,06 | — | 260 | 302 |

1) Combustible; 2) oxidizer; 3) oxygen; 4) fluorine; 5) combustion products; 6) heat of combustion, kcal/kg; 7) molecular weight of combustion products; 8) boiling point of combustion products, °C; 9) density, $g/cm^3$; 10) specific thrust, kg sec/kg; 11) low; 12) high; 13) hydrogen; 14) lithium; 15) beryllium; 16) boron; 17) hydrogen; 18) manganese; 19) aluminum; 20) silicon; 21) gaseous; 22) solid; 23) negative.

The utilization of metals as additives for a hydrocarbon combustible makes it possible to increase considerably its per-unit-weight and per-unit-volume heat of combustion. Table 197 shows the effect of

TABLE 197

Effect of Beryllium Additives on Heat of Combustion of Kerosene-Nitric Acid Fuel

| 1 Количество присадки бериллия в керосине, % | 2 Теплота сгорания | | Увеличение теплоты сгорания единицы объема, % |
|---|---|---|---|
| | 3 ккал/кг | 4 ккал/л | 5 |
| 0 | 1460 | 1920 | 0 |
| 3,6 | 1790 | 2430 | 26,6 |
| 7,2 | 2130 | 2960 | 54,1 |
| 10 | 2480 | 3520 | 83,3 |

1) Amount of beryllium additive in kerosene, %; 2) heat of combustion; 3) kcal/kg; 4) kcal/liter; 5) increase in heat of combustion per unit volume, %.

a metallic beryllium additive on the heat of combustion of a kerosene plus nitric acid fuel, according to the data of G.E. Langemak.

The drawbacks of metal fuels include their high molecular weight and the low heat capacity of the combustion products. This is responsible for the high combustion temperatures and considerable energy losses owing to dissociation of the combustion products. As a result, the efficiency of metal combustibles is decreased.

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[Footnote]

844 In the future, this will be called "dimethylhydrazine."

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[List of Transliterated Symbols]

816 ЖРД = ZhRD = zhidkostnyy raketnyy dvigatel' = liquid rocket motor

820 уд = ud = udel'niy = specific

820 к = k = kamera = chamber

835 Ф = F = furfurilovyy spirt = furfuryl alcohol

## Chapter 26

## OXIDIZERS FOR LIQUID-FUEL ROCKET ENGINES

Oxidizers for ZhRD are the components of the rocket fuels whose function is to oxidize the combustible substances in the engine's combustion chamber. The properties of a rocket fuel are determined basically by the properties of the oxidizer, since much more (approximately 2-4 times) oxidizer than combustible is used in a ZhRD.

Oxidizers may be classified as follows:

- liquid oxygen and ozone;
- concentrated hydrogen peroxide;
- nitric acid and oxides of nitrogen;
- tetranitromethane;
- liquid fluorine and fluorine compounds;
- perchloric acid and oxides of chlorine.

Table 198 lists the most characteristic fuel components that have been employed in foreign rocket engineering.

### OXYGEN AND OZONE

#### Liquid Oxygen

The use of liquid oxygen as an oxidizer was first proposed in 1903 by K.Ye. Tsiolkovskiy [3]. This is one of the most powerful oxidizers. Liquid oxygen is used basically in medium- and long-range rockets, which are loaded with oxidizer immediately prior to launching.

In the USA, liquid oxygen is used as an oxidizer in the engines of the "Redstone," "Jupiter," "Thor," "Atlas" (Fig. 264) and other

rockets. Methyl and ethyl alcohols as well as kerosene-type hydrocarbons are used as combustibles with liquid oxygen. As a rule, fuels based on liquid oxygen are not hypergolic.

The basic energy characteristics of certain types of liquid-oxygen- and ozone-based fuels are listed in Table 199.

Under normal conditions, oxygen is a gas. Its critical temperature and pressure are, respectively, $t_{kr} = -118.8^{\circ}$ and $P_{kr} = 49.7$ atm. Liquid oxygen is a bluish liquid with a specific gravity of 1.14, boiling at $-183^{\circ}$ and freezing at $-219^{\circ}$ [6, 8].

The viscosity of liquid oxygen at the boiling point is 0.189 centipoise, and its latent heat of vaporization is 1.632 kcal/g·mole.

The vapor pressure of liquid oxygen is shown in Fig. 265 as a function of temperature [6].

The most important advantages of liquid oxygen as an oxidizer, in addition to its high energy characteristics, are its nontoxicity, low production cost, and practically unlimited availability.

Liquid oxygen is obtained from air, which is liquefied by alternating cycles of compression and cooling, with the result that its temperature is depressed to $-180^{\circ}$. The liquid air is then rectified: at a temperature of about $-190^{\circ}$, the nitrogen evaporates from it and the liquid oxygen remains [7].

The oxygen content in the technical product may be no lower than 99.0% [9].

At atmospheric pressure, liquid oxygen maintains a constant temperature ($-183^{\circ}$) as a result of the continuous vaporization that takes place with absorption of heat. Evaporation of 1 kg of liquid oxygen requires expenditure of 51 kcal of heat [9].

One of the most serious shortcomings of liquid oxygen is its low boiling point and, consequently, the large evaporation losses during

TABLE 198

Certain Fuel Components That Have Been Used in the Rocket Engineering of Capitalist Countries [8, 33]

| 1 Окислитель | 2 Горючее | 3 Ракета | 4 Класс ракеты | 5 Тяга двигателей, т | 6 Дальность, км |
|---|---|---|---|---|---|
| 7 Жидкий кислород | 8 Этиловый спирт | 9 А-4 ФРГ | 10 Земля — земля | 26,0 | 320 |
| 11 То же | 11 То же | 12 «Редстоун» (США) | 11 То же | 33,7 | 320 |
| » | 13 Керосин | 14 «Юпитер» (США) | » | 70,0 | 2400 |
| » | » | 15 «Тор» (США) | » | 72,5 | 2400 |
| » | 16 Топливо JP-4 | 17 «Атлас» (США) | » | 2×75+ +1×30 | 8800 |
| 18 Азотная кислота | 19 «Тонка-250» | 20 «Х-4» (ФРГ) | 21 Воздух — воздух | 0,12 | 6 |
| 11 То же | 22 Моноэтиловый анилин | 23 «Корпорал» (США) | 10 Земля — земля | 9,0 | 120 |
| » | 24 Газойль | 25 «Вероника» (Франция) | 11 То же | 4,0 | 240 |
| » | 26 Керосин | 27 «Найк-Аякс» (США) | 28 Земля — воздух | 2,27 | 27 |
| » | » | 29 «Эрликон-54» (Швейцария) | 11 То же | 1,0 | 20 |
| » | 30 Несимметричный диметилгидразин | 31 «Авангард», 2-я ступень (США) | Для запуска искусственного спутника | 3,4 | — |
| » | 33 Кеплидин | 34 «Х-17» (США) | 32 Земли — | 23,0 | — |
| 37 Перекись водорода + + перманганат кальция | — | 35 «Хеншель-294» (ФРГ) | 36 Воздух — земля | 1,2 | 10 |
| 38 Перекись водорода | Метиловый спирт 57% + гидразин-гидрат 30% 39 + 13% воды | Истребитель 40 «Ме-163-В» (ФРГ) | — | 1,7 | — |
| 11 То же | 41 Метиловый спирт + гидразин | 42 «TR» (Англия) | 43 Аэродинамические последования | 0,4 | 35 |
| » | 44 Керосин | 45 «SX-45» (Англия) | 28 Земля — воздух | — | — |
| » | » | 46 «Управляемая бомба» (Англия) | Воздух — 36 земля | 3,6 | — |

1) Oxidizer; 2) combustible; 3) rocket; 4) class of rocket; 5) engine thrust, tons; 6) range, km; 7) liquid oxygen; 8) ethyl alcohol; 9) A-4, Federal Republic of Germany; 10) surface-to-surface; 11) same; 12) "Redstone" (USA); 13) kerosene; 14) "Jupiter" (USA); 15) "Thor" (USA); 16) JP-4 fuel; 17) "Atlas" (USA); 18) nitric acid; 19) "Tonka-250"; 20) "X-4" (Federal Republic of Germany); 21) air-to-air; 22) monoethylaniline; 23) "Corporal" (USA); 24) gas oil; 25) "Veronica" (France); 26) kerosene; 27) "Nike-Ajax" (USA); 28) surface-to-air; 29) "Erlikon-54" (Switzerland); 30) unsymmetrical dimethylhydrazine; 31) "Vanguard,"

Table 198 key (continued)

second stage (USA); 32) for launching of artificial earth satellite; 33) xylidine; 34) "X-17" (USA); 35) "Henschel-294" (Federal Republic of Germany), 36) air-to-surface; 37) hydrogen peroxide + calcium permanganate; 38) hydrogen peroxide; 39) 57% methyl alcohol + 30% hydrazine hydrate + 13% water; 40) "Me-163-B" (Federal Republic of Germany); 41) methyl alcohol + hydrazine; 42) "TR" (England); 43) aerodynamic research; 44) kerosene; 45) "SX-45" (England); 46) "guided bomb" (England).

TABLE 199

Basic Energy Characteristics of Fuels Based on Liquid Oxygen and Ozone [4, 5]

| | 1 Топливная смесь | 2 Отношение окислителя к горючему | 3 Плотность топлива, кг/л | 4 Давление в камере сгорания $P_к$, кг/см² | 5 Температура в камере сгорания, °С | 6 Удельная тяга, кг сек/кг |
|---|---|---|---|---|---|---|
| 7 | Кислород + жидкий водород | 5,3 | 0,33 | 24 | 2650 | 335 |
| 8 | Кислород + аммиак | 1,4 | 0,98 | 21 | 2730 | 255 |
| 9 | Кислород + гидразин | 0,67 | 1,09 | 21 | 2800 | 267 |
| 10 | Кислород + этиловый спирт | 1,5 | 0,98 | 28 | 2980 | 232 |
| 11 | Кислород + газолин | 2,5 | 0,965 | 21 | 3000 | 242 |
| 12 | Кислород + метиламин | 1,6 | 0,91 | 28 | 3015 | 248 |
| 13 | Кислород + несимметричный диметилгидразин | 1,4 | 0,96 | 28 | 3120 | 249 |
| 14 | Кислород + топливо JP-4 | 2,2 | 0,98 | 28 | 3250 | 240 |
| 15 | Кислород + углеводородное горючее (C : H = 6) | 2,3 | 0,98 | 28 | 3190 | 247 |
| 16 | Озон + углеводородное горючее (C : H = 6) | 2,4 | 1,14 | 28 | 3525 | 260 |
| 17 | Кислород (70%) и озон (30%) + + углеводородное горючее (C : H = 6) | 2,3 | 1,04 | 28 | 3200 | 252 |

1) Fuel mixture; 2) oxidizer-to-fuel ratio; 3) fuel density, kg/liter; 4) combustion-chamber pressure $P_k$, kg/cm$^2$; 5) combustion-chamber temperature, °C; 6) specific thrust, kg·sec/kg; 7) oxygen + liquid hydrogen; 8) oxygen + ammonia; 9) oxygen + hydrazine; 10) oxygen + ethyl alcohol; 11) oxygen + gasoline; 12) oxygen + methylamine; 13) oxygen + unsymmetrical dimethylhydrazine; 14) oxygen + JP-4 fuel; 15) oxygen + hydrocarbon combustible (C:H = 6); 16) ozone + hydrocarbon combustible (C:H = 6); 17) oxygen (70%) and ozone (30%) + hydrocarbon combustible (C:H = 6).

storage and shipment.

As a result, the basic problem in using liquid oxygen and par-

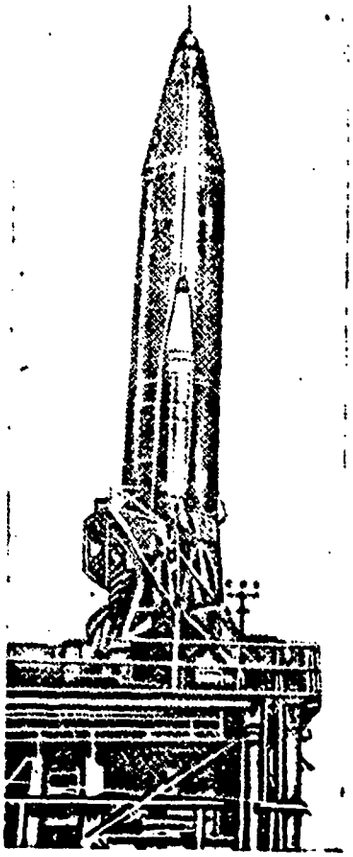

Fig. 264. "Atlas" intercontinental ballistic rocket (USA).

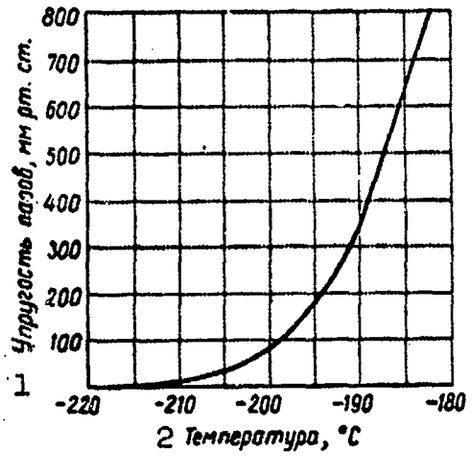


Fig. 265. Vapor pressure of liquid oxygen as a function of temperature. 1) Vapor pressure, mm Hg; 2) temperature, °C.

ticularly in storing it consists in minimizing the evaporation losses as far as possible.

Liquid oxygen is stored in special containers with excellent heat insulation. The evaporation rate of oxygen depends on the size of the heated surface and the thermal-conductivity coefficient of the insulation. Since a sphere has the smallest surface area, relatively small containers for storage of liquid oxygen are, as a rule, made spherical. Larger containers are normally given cylindrical shapes.

Heat insulation is provided for storage of liquid oxygen either by creating a deep vacuum (below 0.001 mm Hg) in the space between the inside and outside walls of the container or by pouring a heat-insulating material into all spaces between the walls of the vessels holding the oxygen and the outside cases of the storage capacity. Loose magnesium carbonate powder, asbestite, magnesium cement, slag or glass wool and other materials are used as heat insulators [9, 10].

Magnesium carbonate powder has the lowest thermal-conductivity coefficient, which is 0.027 kcal/m·hour·°C [7]. When vacuum heat insulation is used, the oxygen losses are about 25% smaller than when heat-insulating materials are employed [10]. The best effect is secured by using the so-called vacuum-powder heat insulation, a practice consisting in pouring the space between the outside and inside walls of the liquid-oxygen vessel full of magnesium carbonate powder and then evacuating the air from this space to produce a high vacuum. The oxygen losses due to evaporation when the slag-wool heat insulation is employed represent 3-5% per day, while they drop to less than 1% per day for vacuum and vacuum-powder insulation [10]. High moisture content and the presence of cracks in the heat insulation result in a considerable increase in its thermal conductivity and, consequently, in evaporation losses of oxygen.

Under laboratory conditions, liquid oxygen is stored in Dewar flasks. When considerable quantities of liquid oxygen are to be stored or shipped, special metallic reservoirs known as "tanks" and having capacities from 1 to 50 $m^3$ are employed. In isolated cases, the capacity may run up to 40,000-45,000 $m^3$ [9]. The larger the capacity of the liquid-oxygen vessel, the smaller will be its relative evaporation losses expressed in per cent. The literature [12] describes a plan for an underground reservoir to hold 1 million tons of liquid oxygen. This reservoir is a cylindrical tank 103.5 m in diameter and 119 m high provided with heat insulation 10 m thick. The evaporation losses of oxygen in such a reservoir would be only about 0.001% per day.

Special oxygen tank cars are used for railroad shipment of liquid oxygen. Special mobile fueling units are employed for hauling liquid oxygen over short distances and feeding it to rockets.

Since shipment of liquid oxygen over considerable distances results in large evaporation losses, it is frequently advisable to produce the liquid oxygen at the point of consumption. Special mobile apparatus for production of liquid oxygen have been built for these purposes. In the USA, for example, there is a unit with an output of 5 tons/day of liquid oxygen for servicing the "Redstone" rockets; this is carried on two trailers and adapted for air transport.

A unit has also been developed for an output of 20 tons/day of pure (99.5%) liquid oxygen; this one is mounted on four trailers.

The unit operates on diesel fuel, of which 0.5 kg is required to produce 1 kg of liquid oxygen. The liquid oxygen produced by the unit is supercooled and then drained into special tanks or mobile fueling units [13].

Containers for storage and shipment of liquid oxygen may be equipped with special automatic helium coolers to reflux-condense the evaporated oxygen; in these devices, liquid helium ($t_k = -269^\circ$) circulates through a tubular condenser installed in the top of the reservoir holding the liquid oxygen. The helium coolers make it possible to store liquid oxygen for long periods and ship it over long distances without losses [9].

Copper and copper alloys, aluminum and stainless chrome-nickel steels are used in fabricating equipment for the storage, shipment and transfer of liquid oxygen.

Carbon steel and cast iron are not suitable for these purposes, since they become extremely brittle on contact with liquid oxygen [6]. Copper, aluminum and lead are used as packing materials. The fire hazard prohibits the use of lubricants and oils of organic origin in work with liquid oxygen. Various types of impurities accumulate gradually during storage and transfer of liquid oxygen; these include

acetylene, mineral oils, carbon dioxide, water and others. The presence of water and carbon dioxide in the form of a solid phase in oxygen may result in clogging of filters and various parts of the plumbing when the oxidizer is transferred. The accumulation of hydrocarbon oils and acetylene, which may result in violent explosion of the entire mass of liquid oxygen, is particularly dangerous. It is necessary to exercise great caution in working with liquid oxygen because organic substances in contact with it and in the atmosphere formed by its saturated vapor may easily self-ignite or form explosive mixtures. Brief contact of liquid oxygen with the skin is not dangerous, since a gas cushion that protects the body from freezing forms between the liquid and the skin as it boils [14]. Touching metals that have been cooled by liquid oxygen is more dangerous.

Ozone

The use of oxygen as a ZhRD oxidizer was first proposed by Yu.V. Kondratyuk [15]. Ozone is one of the strongest oxidizers: paired with liquid hydrogen it develops a larger specific thrust than does liquid fluorine.

Ozone is an allotropic modification of oxygen. Its molecule contains three atoms of oxygen.

Liquid ozone is dark blue in color, boils at a temperature of $-112^{\circ}$ and freezes at $-251^{\circ}$. Its density (1.46 at the boiling point) is considerably higher than those of oxygen and fluorine. Ozone can be produced from oxygen by the action of a corona discharge or by thermal methods based on the fact that oxygen undergoes partial transformation into ozone at high temperatures [6]. The mixture of oxygen with ozone that is produced in this manner is cooled by liquid air, so that liquid ozone or liquid mixtures of oxygen and ozone can be produced.

A diagram of a unit for producing ozone is shown in Fig. 266.

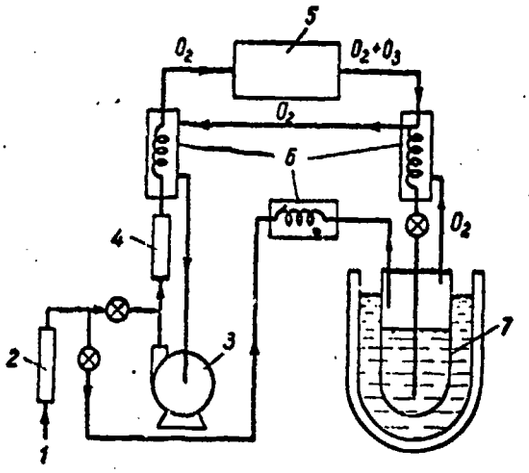


Fig. 266. Diagram of apparatus for production of ozone. 1) Oxygen from bottles; 2) oxygen purifier; 3) recirculation pump; 4) oxygen-feed regulator; 5) ozonator; 6) heat exchangers; 7) solution of ozone in oxygen.

The basic deficiencies of ozone, apart from its low boiling point, include an explosion hazard and high toxicity. Ozone is liable to spontaneous decomposition with evolution of a large quantity of heat, in accordance with the equation

$$2O_3 \rightarrow 3O_2 + 69 \text{ kcal}.$$

Gaseous ozone may decompose explosively [16]. Liquid ozone is stable at room temperature. However, the presence in it of even trace quantities of organic impurities such as lubricating oils makes ozone an extremely explosive material that detonates on heating and mechanical agitation [17]. A necessary condition for the production of explosion-safe liquid ozone is specific and thorough purification of the oxygen used for its production. Ozone explosions begin in the gaseous phase, so that gaseous ozone requires extremely cautious handling.

The use of pure liquid ozone as an oxidizer for ZhRD is still difficult due to its tendency to explosive decomposition. One method of stabilizing ozone is its use in mixture with liquid oxygen. A mixture of ozone with oxygen containing up to 30% of liquid ozone is of practical interest; this mixture does not represent an explosion hazard and is stable in storage [18].

The effectiveness of liquid oxygen as an oxidizer increases in proportion to its ozone content (Fig. 267) [19].

The presence of ozone, which is capable of yielding active nascent oxygen on decomposition, in liquid oxygen contributes to an

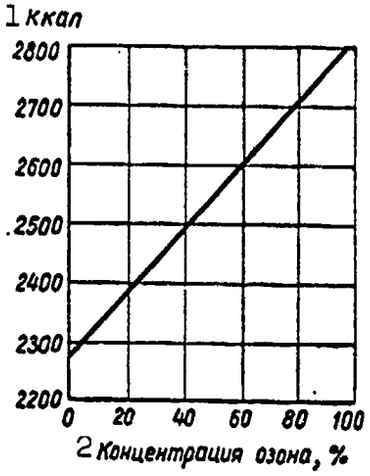


Fig. 267. Heat of combustion of ozone-oxygen mixtures (with toluene) as a function of ozone concentration. 1) Kcal; 2) ozone concentration, %.

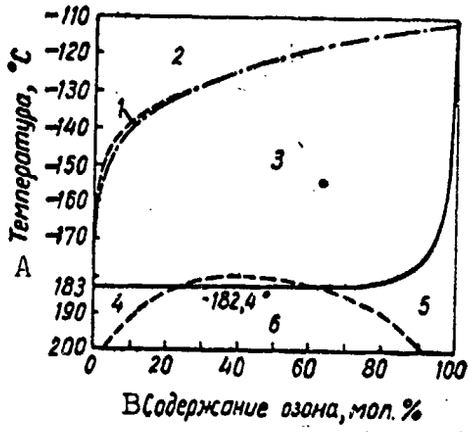


Fig. 268. Diagram of state of ozone-oxygen system at atmospheric pressure. 1) Ideal solution; 2) vapor; 3) liquid and vapor; 4) liquid oxygen; 5) liquid ozone; 6) two liquid phases. A) Temperature, °C; B) ozone content, mole-%.

increase in the combustion rate of fuels in the ZhRD chamber.

Ozone has limited solubility in liquid oxygen. Mixtures containing from 25 to 55% of ozone separate into two liquid phases at a temperature of $-183^{\circ}$: one is rich in ozone (55% $O_3$), while the other has a low ozone content. At temperatures above $-179.5^{\circ}$, ozone mixes with oxygen in all proportions [20]. Figure 268 shows the diagram of state of the ozone-oxygen system [21].

The ozone-enriched layer is explosive. When a mixture of oxygen with ozone is stored, it is necessary to take into account the possibility of an increase in ozone concentration due to the continuous and preferential evaporation of the oxygen, which boils at a lower temperature than ozone.

## CONCENTRATED HYDROGEN PEROXIDE

Concentrated hydrogen peroxide has come into extensive use in rocket engineering as an oxidizer and as an agent for the production of the vapor gas required to drive the turbines of turbopump sets in

TABLE 200

Theoretical Characteristics of Fuels Based on Concentrated Hydrogen Peroxide [4, 5]

| 1 Топливная смесь | 2 Отношение окислителя к горючему | 3 Плотность топлива, кг/л | 4 Давление в камере сгорания, кг/см² | 5 Температура в камере сгорания, °С | 6 Удельная тяга, кг сек/кг |
|---|---|---|---|---|---|
| 7 90%-ная перекись водорода + + гидразин . . . . . | 1,5 | 1,2 | 28 | 2300 | 250 |
| 8 99,6%-ная перекись водорода + гидразин . . . . . | 1,7 | 1,24 | 28 | 2585 | 262 |
| 9 99,6%-ная перекись водорода + топливо JP-4 . . . . . | 6,5 | 1,28 | 28 | 2665 | 238 |
| 10 Безводная перекись водорода + 92,5%-ный этиловый спирт . . . . . | 3,4 | 1,22 | 22 | 2440 | 229 |
| 11 87%-ная перекись водорода + + метиловый спирт . . . . | 3,7 | 1,19 | 22 | 2280 | 225 |
| 12 Перекись водорода (54%) и нитрат аммония (40%) + керосин . . . . . | 2,0 | 1,34 | 28 | 2355 | 228 |

1) Fuel mixture; 2) oxidizer-to-combustible ratio; 3) fuel density, kg/liter; 4) combustion-chamber pressure, $kg/cm^2$; 5) combustion-chamber temperature, °C; 6) specific thrust, kg·sec/kg; 7) 90% hydrogen peroxide + hydrazine; 8) 99.6% hydrogen peroxide + hydrazine; 9) 99.6% hydrogen peroxide + JP-4 fuel; 10) anhydrous hydrogen peroxide + 92.5% ethyl alcohol; 11) 87% hydrogen peroxide + methyl alcohol; 12) hydrogen peroxide (54%) and ammonium nitrate (40%) + kerosene.

certain types of rockets.

In 1944, hydrogen peroxide was used by the Germans as a vapor-gas source in the A-4 (V-2) rocket. Hydrogen peroxide is used for the same purpose in the American Redstone, Viking, Jupiter and other rockets. Concentrated hydrogen peroxide has been used as an oxidizer in the engine of the Me-163B interceptor aircraft, as well as in certain British and American ZhRD types [22, 23, 24].

Low-water hydrogen peroxide (90-95%) yields nothing to nitric acid in efficiency, although it contains less active oxygen. For example, the energy properties of a fuel mixture consisting of 90% hydrogen peroxide and kerosene approach those of such fuels as red fuming nitric acid + aniline and liquid oxygen + ethyl alcohol [4]. This is

accounted for by the fact that the hydrogen peroxide molecule decomposes with evolution of considerable heat before entering into the oxidation reaction; this delivers an additional heat effect when the fuel is burned in the combustion chamber.

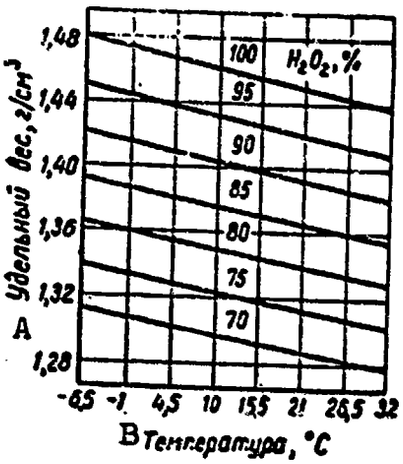


Fig. 269. Specific gravity of hydrogen peroxide as a function of its concentration and temperature. A) Specific gravity, $g/cm^3$; B) temperature, °C.

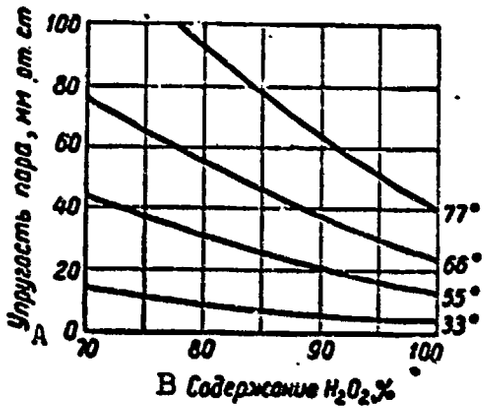


Fig. 270. Vapor pressure of hydrogen peroxide as a function of concentration and temperature. A) Vapor pressure, mm Hg; B) $H_2O_2$ content, %.

TABLE 201

Physical Properties of Hydrogen Peroxide [6, 22, 25]

| 1 Показатели | 2 Концентрация $H_2O_2$, % | | |
|---|---|---|---|
| | 80 | 90 | 100 |
| 3 Плотность при 18°С | 1.35 | 1.39 (25°) | 1.44 |
| 4 Температура замерзания, °С | —22.9 | —9.4 | —0.89 |
| 5 Температура кипения (теоретическая), °С | — | 140 | 151.4 |
| 6 Вязкость при 18°С, сст | 1.307 (15.5°) | 1.30 | 1.307 |
| 7 Показатель преломления | — | 1.398 | 1.414 |
| 8 Поверхностное натяжение, дин/см | 75.3 | 75.5 | 75.7 |
| 9 Теплоемкость, кал/г | 0.64 | 0.58 | 0.57 |
| 10 Теплота образования жидкой $H_2O_2$, ккал/г-моль | 76.8 | 59.8 | 43.2 |

1) Index; 2) $H_2O_2$ concentration, %; 3) density at 18°C; 4) freezing point, °C; 5) boiling point (theoretical), °C; 6) viscosity at 18°C, centistokes; 7) refractive index; 8) surface tension, dynes/cm; 9) heat capacity, cal/g; 10) heat of formation of liquid $H_2O_2$, kcal/g-mole.

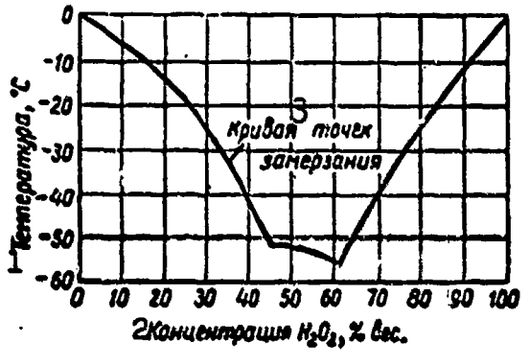


Fig. 271. Diagram of state of $H_2O_2$-$H_2O$ system. 1) Temperature, °C; 2) concentration of $H_2O_2$, % by weight; 3) freezing-point curve.

Table 200 lists certain theoretical characteristics for fuels based on concentrated hydrogen peroxide [4, 5].

Hydrogen peroxide can be produced by various methods [22]. The electrochemical method consists in electrolyzing aqueous solutions of sulfuric acid; the result is formation of persulfuric acid, which is then hydrolyzed by water vapor with formation of dilute aqueous solutions of hydrogen peroxide (perhydrol). The concentrated hydrogen peroxide is produced by two-staged rectification of the solution in special columns, which yields commercial-grade 80-90% hydrogen peroxide.

Low-water hydrogen peroxide is a colorless transparent liquid with an extremely faint odor reminiscent of those of nitrogen oxides.

The physical properties of hydrogen peroxide of various concentrations are given in Table 201.

Figures 269 and 270 indicate the specific gravity and vapor pressure of hydrogen peroxide as functions of its concentration and temperature.

Hydrogen peroxide is regarded as an extremely weak acid that cannot even be detected by litmus-paper testing. The dissociation constant of hydrogen peroxide in the equation $H_2O_2 \rightleftarrows H^+ + HO_2^-$ is $2.4 \cdot 10^{12}$ at a temperature of 25°C.

Hydrogen peroxide mixes in all proportions with water and ethyl and methyl alcohols.

One shortcoming of concentrated hydrogen peroxide is its high

freezing point, which makes it difficult to work with in winter.

Figure 271 shows a diagram of phase state for the $H_2O_2$-$H_2O$ system [22].

Solutions of 55-60% concentration have the lowest freezing points. Concentrated hydrogen peroxide has the ability to supercool. For example, pure 90% hydrogen peroxide may be supercooled to $-15^\circ$ even during agitation. Effective additives that would make it possible to reduce the freezing point of hydrogen peroxide by any considerable amount without detriment to its energy properties have not yet been found. Figure 272 shows the influence of ammonium-nitrate additives to 90% hydrogen peroxide on the latter's freezing point.

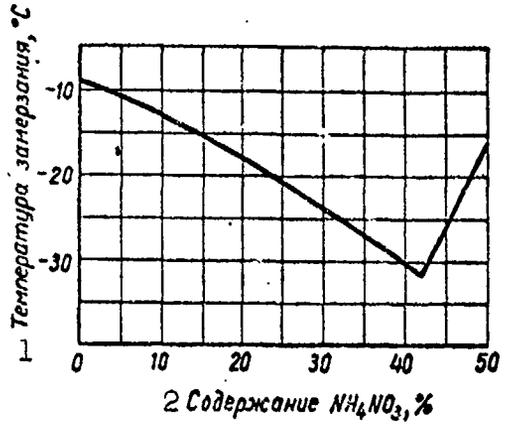


Fig. 272. Freezing points of hydrogen-peroxide solutions of ammonium nitrate. 1) Freezing point, °C; 2) $NH_4NO_3$ content, %.

The mixture consisting of 40% $NH_4NO_3$ and 60% $H_2O_2$ has the lowest freezing point at $-32^\circ$ [4].

A distinguishing property of low-water hydrogen peroxide, and a considerable disadvantage from the standpoint of storage, is its thermal instability and high sensitivity to various types of contamination. On heating, and under the action of various catalysts, hydrogen peroxide decomposes with evolution of heat in accordance with the equation

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 + 23{,}45 \text{ kcal}.$$

The decomposition rate of 90% hydrogen peroxide as a function of temperature is indicated in Table 202.

Absolutely pure low-water hydrogen peroxide may be stored at normal temperatures for extremely long periods without noticeable decomposition. Contamination by various impurities (dust, rust, salts of

TABLE 202

Stability of 90% Hydrogen Peroxide at Various Temperatures [9]

| Температура, °С 1 | 2 Приближенная скорость разложения |
|---|---|
| 30 | 3 1% в год |
| 66 | 4 1% в неделю |
| 100 | 5 2% в сутки |
| 140 | 6 Быстро разлагается, вскипая |

1) Temperature, °C; 2) approximate decomposition rate; 3) 1% per year; 4) 1% per week; 5) 2% per day; 6) decomposes rapidly with bumping.

heavy metals, alkalis, enzymes, and so forth) result in a sharp increase in the decomposition rate of hydrogen peroxide and severe overheating. At a temperature of 140-150°, the decomposition becomes explosive. The influence of certain impurities on the stability of 90%

TABLE 203

Influence of Impurities on Decomposition Rate of 90% Hydrogen Peroxide at Temperature of 100°C During 24 Hours [22]

| 1 Примеси | 2 Количество примеси, мг/л | 3 Потери активного кислорода, % |
|---|---|---|
| 4 Без примесей | — | 2 |
| 5 Алюминий | 10 | 2 |
| 6 Хром | 0,1 | 96 |
| 7 Медь | 0,01 | 24 |
| " | 0,1 | 85 |
| 8 Железо | 1,0 | 15 |
| 9 Олово | 10 | 3 |
| 10 Цинк | 10 | 10 |

1) Impurity; 2) quantity of impurity, mg/liter; 3) loss of active oxygen, %; 4) without impurities; 5) aluminum; 6) chromium; 7) copper; 8) iron; 9) tin; 10) zinc.

hydrogen peroxide is shown in Table 203.

Permanganates, manganese dioxide, cuprous cyanide salts and others are strong catalysts for the decomposition of hydrogen peroxide.

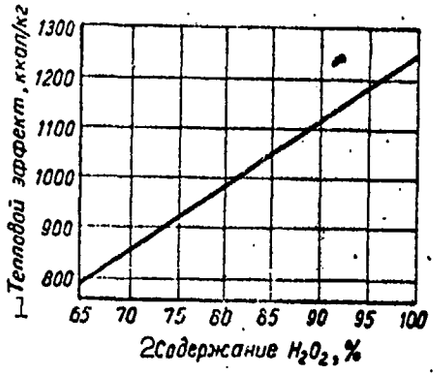


Fig. 273. Heat effect of decomposition reaction of hydrogen peroxide as a function of its concentration. 1) Heat effect, kcal/kg; 2) $H_2O_2$ constant, %.

A considerable quantity of heat is evolved in the decomposition of hydrogen peroxide.

The dependence of the heat effect of the decomposition on the concentration of the hydrogen peroxide is shown in Fig. 273.

Decomposition of 1 kg of 90% hydrogen peroxide liberates 1700 liters of vapor gas heated to 740° and containing 0.423 kg of active oxygen.

The ability of hydrogen peroxide to decompose rapidly under the influence of catalysts, with evolution of heat and formation of a large quantity of gaseous decomposition products, makes it possible to use it as a monopropellant fuel.

The instability of hydrogen peroxide and its sensitivity to various impurities were for a long time serious obstacles to its widespread use in engineering. Many studies were undertaken to find ways to stabilize hydrogen peroxide, with the result that it was established that orthophosphoric and pyrophosphoric acids and their salts, stannic acid and its salts, hydroxyquinoline and other agents may be used as stabilizers [4, 9, 22]. Orthophosphoric acid, stannates and pyrophosphates have come into practical use. Thus, when 23 mg/liter of orthophosphoric acid are added to 87% hydrogen peroxide, its stability is improved considerably [9]. The action of the stabilizer depends on its nature and the nature of the contamination. No universal stabilizer for hydrogen peroxide has as yet been found. For example, the catalytic action of copper ions is weakened considerably by stannic acid and its salts, while that of chromium ions is countered by orthophosphoric acid and pyrophosphates.

The best guaranty for stability of hydrogen peroxide is to safeguard its purity in production, storage, shipping and transfer. When a small quantity of harmful impurities gets into hydrogen peroxide, stabilizers are sufficiently effective, but the decomposition process cannot be retarded by any stabilizer if the impurities are present in large amounts. With rising temperature, the sensitivity of hydrogen peroxide to the catalyzing action of impurities increases. Concentrated hydrogen peroxide is stored and shipped in special containers (tanks, tank cars, drums) made from pure aluminum (Fig. 274). In isolated cases, stainless steel may be used. Polyvinyl chloride plastic is used as a gasketing and stuffing material. Teflon and, to a lesser degree, polyethylene are also stable against hydrogen peroxide [26, 27].

To raise the stability of hydrogen peroxide in storage, the inside surfaces of the aluminum reservoirs and drums, as well as those of the pumps and piping systems are given special treatment (passivated) by dilute alkali and nitric-acid solutions.

The storage losses due to decomposition of the hydrogen peroxide should not exceed 1% per year [28]. The stability of hydrogen peroxide in storage is checked by regular temperature measurements.

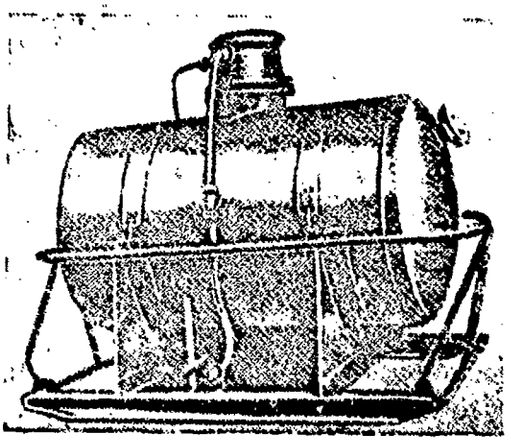

Fig. 274. Tank for storage of hydrogen peroxide.

If rapid heating of the product is detected, an additional small quantity of stabilizer is injected into it. If this is not adequate, the hydrogen peroxide is diluted with water to safe concentration (67%) [29].

Concentrated hydrogen peroxide causes dot corrosion of aluminum. A corrosion inhibitor is added to hydrogen peroxide to reduce its

corrosive action on metals.

Great caution is required in handling hydrogen peroxide. If it comes into contact with combustible materials (grass, straw, textiles, paper, wood, and so forth), concentrated hydrogen peroxide decomposes with evolution of a large amount of heat, so that these materials burst into flame.

Mixtures of concentrated hydrogen peroxide with organic substances (benzene, toluene, alcohols and others) are highly explosive materials. If such mixtures are accidentally formed in work with hydrogen peroxide, they should be disarmed immediately by dilution with a large quantity of water [4].

Contact of concentrated hydrogen peroxide with the skin produces severe burns. Contact with the eyes may result in blindness. The best first aid in this case is copious water washing of the affected areas.

Hydrogen peroxide vapor irritates and inflames. Its decomposition products are not toxic. Protective clothing – polyvinyl chloride coveralls or an apron, boots and gloves – are worn in work with hydrogen peroxide.

## OXIDIZERS BASED ON NITRIC ACID AND NITROGEN OXIDES

### Nitric Acid

Concentrated nitric acid was first proposed as an oxidizer in the USSR. The widespread use of nitric acid in rocket engineering despite its relatively low energy properties is accounted for by the following factors:

– at normal temperatures, nitric acid is in the liquid state, which makes it easier to work with and, specifically, makes it possible to hold a rocket fueled and fully ready for launching for long periods of time;

– nitric acid is a readily available and cheap product with a

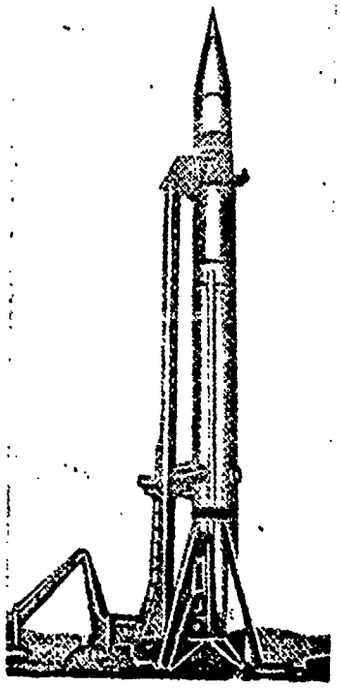

Fig. 275. Short-range "Corporal" ballistic rocket (USA).

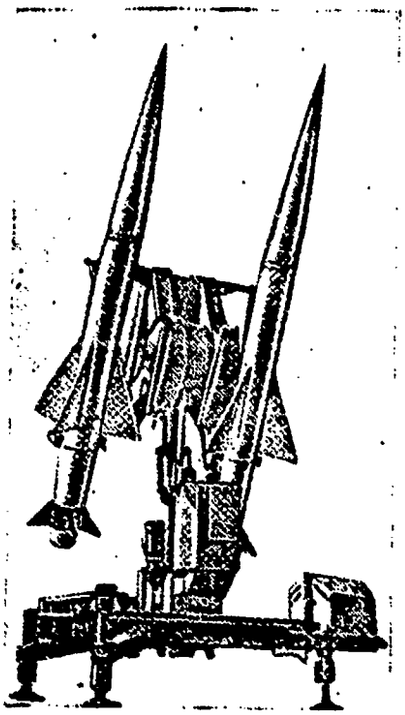

Fig. 276. "Erlikon-54" antiaircraft rocket on twinned launcher (Switzerland).

practically unlimited raw-material base and is in mass production by the chemical industry;

– with a number of combustibles (aniline, xylidine, furfuryl alcohol and others), nitric acid forms hypergolic mixtures that do not require a special device for ignition in the ZhRD combustion chamber [31, 32].

Concentrated nitric acid is used as an oxidizer in many rockets: the "Vanguard," "Corporal" (Fig. 275), "Nike-Ajax," "Jupiter" (USA), "Veronica" (France), "Erlikon-54" (Switzerland) (Fig. 276) and others [33].

Nitric acid is used in combination with various combustibles: aniline, xylidine, hydrazine, unsymmetrical dimethyl hydrazine, "Tonka-250" (a mixture of xylidine with triethylamine in 1:1 proportions), kerosene and others [8, 33].

TABLE 204

Energy Properties of Fuels Based on Nitric Acid [4, 5]

| 1 Топливная смесь | 2 Отношение окислителя к горючему | 3 Плотность топлива, кг/л | 4 Давление в камере сгорания $P_к$, кг/см² | 5 Температура в камере сгорания, °С | 6 Удельная тяга, кг сек/кг |
|---|---|---|---|---|---|
| 7 Азотная кислота + жидкий водород | 12,6 | 0,61 | 21 | 2930 | 298 |
| 8 Азотная кислота + гидразин | 1,6 | 1,28 | 21 | 2390 | 243 |
| 9 Азотная кислота (85%) и четырехокись азота (15%) + + гидразин | 1,3 | 1,26 | 28 | 2750 | 247 |
| 10 Азотная кислота + фурфуриловый спирт | 1,9 | 1,37 | 21 | 2110 | 214 |
| 11 Азотная кислота (78%) и четырехокись азота (22%) + + аммиак | 2,15 | 1,12 | 28 | 2325 | 230 |
| 12 Азотная кислота (78%) и четырехокись азота (22%) + + несимметричный диметилгидразин | 2,6 | 1,23 | 28 | 2870 | 241 |
| 13 Азотная кислота + анилин | 3,0 | 1,37 | 21 | 2770 | 221 |
| 14 Азотная кислота (78%) и четырехокись азота (22%) + + диэтилентриамин (80%) в смеси с метиламином (20%) | 3,0 | 1,33 | 28 | 2900 | 240 |
| 15 Меланж ($HNO_3$ — 90%, $H_2SO_4$ — 10%) + моноэтиланилин | 4,55 | 1,396 | 24 | 2060 | 210 |
| 16 Четырехокись азота + гидразин | 1,1 | 1,2 | 28 | 2730 | 250 |

1) Fuel mixture; 2) oxidizer-to-combustible ratio; 3) density of fuel, kg/liter; 4) combustion chamber pressure $P_k$, kg/cm$^2$; 5) combustion-chamber temperature, °C; 6) specific thrust, kg·sec/kg; 7) nitric acid + liquid hydrogen; 8) nitric acid + hydrazine; 9) nitric acid (85%) and nitrogen tetroxide (15%) + hydrazine; 10) nitric acid + furfuryl alcohol; 11) nitric acid (78%) and nitrogen tetroxide (22%) + ammonia; 12) nitric acid (78%) and nitrogen tetroxide (22%) + unsymmetrical dimethyl hydrazine; 13) nitric acid + aniline; 14) nitric acid (78%) and nitrogen tetroxide (22%) + diethylene triamine (80%) mixed with methylamine (20%); 15) melange (90% $HNO_3$, 10% $H_2SO_4$) + monoethyl aniline; 16) nitrogen tetroxide + hydrazine.

Calculated energy characteristics of fuels based on nitric acid are listed in Table 204.

On an industrial scale, nitric acid is produced by oxidation of ammonia by atmospheric oxygen in contact apparatus with a platinum

catalyst. The nitric oxide formed in this process is further oxidized in special towers and autoclaves, first to nitrogen dioxide and then to nitric acid.

The ammonia used for production of nitric acid is obtained by direct synthesis from atmospheric nitrogen and hydrogen, the latter formed by passing water vapor through glowing coke ("water gas") [34]. In the last analysis, therefore, nitric acid is produced from air and water, i.e., its raw-material resources are virtually unlimited.

Chemically pure nitric acid is a heavy colorless liquid (density 1.52) that boils at a temperature of 86° and freezes at –41.2°. Its heat of formation is +42.4 kcal/mole and its heat capacity is 0.425 kcal/mole. Anhydrous nitric acid is unstable even at subzero temperatures, decomposing in accordance with the equation

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2.$$

As a result, concentrated nitric acid always contains a certain amount of water and oxides of nitrogen. The chemical industry produces technical 96-98% nitric acid, which is often referred to as the "white fuming acid." This is a heavy straw-yellow liquid with a density of 1.49-1.50 at a temperature of 20°. It "fumes" in air due to the formation of fine droplets of dilute acid with the atmospheric moisture. The viscosity of the 96-98% acid varies from 2.0 to 0.7 centipoise in the temperature range from –20° to 50°C. The freezing point depends on the composition of the acid. The 98.8% nitric acid freezes at –42.3°. With diminishing concentration, its freezing point is depressed, reaching –68.5° for 90% nitric acid [6, 35].

Nitric acid is virtually immiscible with the majority of hydrocarbons. Alcohols, nitrobenzene, dichloroethane, ethyl nitrate and other nitro- and halogen derivatives show excellent solubility in concentrated nitric acid. Here, extremely high-explosive mixtures are

TABLE 205

Physical Properties of Oxidizers Based on Nitric Acid (USA) [36]

| 1 Показатели | WFNA | RFNA |
|---|---|---|
| 2 Температура кипения, °С | 87,8 | 65,6 |
| 3 Температура замерзания, °С | −47 | 4 Ниже −50 |
| 5 Плотность при 20°, г/см³ | 1,50 | 1,57 |
| 6 Вязкость при 20°, сст | 0,54 | 0,89 |
| 7 Упругость паров при 20°, мм рт. ст. | 44 | 133 |
| 8 Теплоемкость, ккал/моль | 0,42 | 0,39 |

Note. In the USA, nitric-acid based oxidizers are produced to conform to Specifications MPD-579 and MPD-25508.

1) Index; 2) boiling point, °C; 3) freezing point, °C; 4) below −50; 5) density at 20°, g/cm$^3$; 6) viscosity at 20°, cst; 7) vapor pressure at 20°, mm Hg; 8) heat capacity kcal/mole.

formed. Water mixes with nitric acid in all proportions. To increase the effectiveness of concentrated nitric acid as an oxidizer and to improve its thermal stability, it is frequently used in mixtures with nitrogen tetroxide (about 20% by weight) [35]. Such a mixture has higher oxidizing properties and a higher density than 96-98% nitric acid. The nitrogen tetroxide in nitric-acid-base oxidizers undergoes partial dissociation by the equation $N_2O_4 \rightleftarrows 2NO_2$. Here, the relative content of nitrogen dioxide increases with increasing temperature. The brown coloration of nitric-acid-base oxidizers is due to the presence of free nitrogen dioxide in them. Nitrogen tetroxide shows good solubility in concentrated nitric acid, but only up to a certain concentration limit above which the system separates at a given temperature. For example, only about 55% of nitrogen tetroxide dissolves in nitric acid at a temperature of 18-20° [6]. Acid containing up to 20% of nitrogen oxides is known as "red fuming nitric acid." This is a heavy orange-brown liquid that fumes heavily in air as a result of evolution of brown nitrogen dioxide vapor.

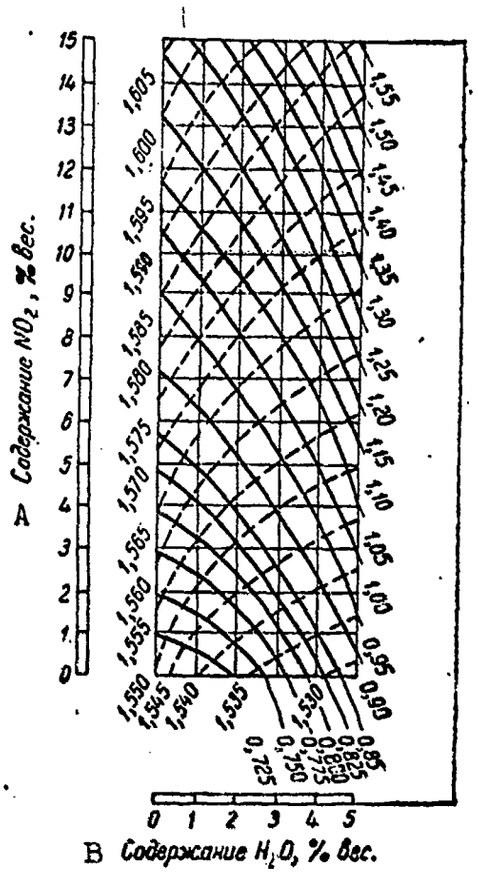


Fig. 277. Density and kinematic-viscosity curves for the $HNO_3$-$NO_2$-$H_2O$ system at 0°C. ——— Kinematic viscosity in cst; — — — density in g/cm$^3$. A) $NO_2$ content, % by weight; B) $H_2O$ content, % by weight.

In the USA, the white and red fuming acids are used as oxidizers under the designations WFNA and RFNA. The oxidizer WFNA represents 96-98% nitric acid, while RFNA contains approximately 15% of nitrogen oxides and 3% of water [36]. The physical properties of these oxidizers are listed in Table 205.

The density of oxidizers based on nitric acid depends on their composition and temperature [37]. On addition of water, the density diminishes, while it increases with increasing content of nitrogen tetroxide (Figs. 277 and 278).

An alignment chart (Fig. 278) may be used to determine the concentration of water in the oxidizer from the specific gravity of the oxidizer and its nitrogen-oxide content.

The vapor pressures of oxidizers based on nitric acid also depend on their composition and temperature (Fig. 279) [37].

With increasing content of nitrogen oxides in nitric acid, its vapor pressure rises sharply. Addition of water to nitric acid that contains a small quantity of nitrogen oxides results in depression of the acid's vapor pressure. On the other hand, increasing the water content in the $HNO_3$-$N_2O_4$-$H_2O$ system when the nitrogen tetroxide concentration is high (10-20%) results in a considerable rise in the

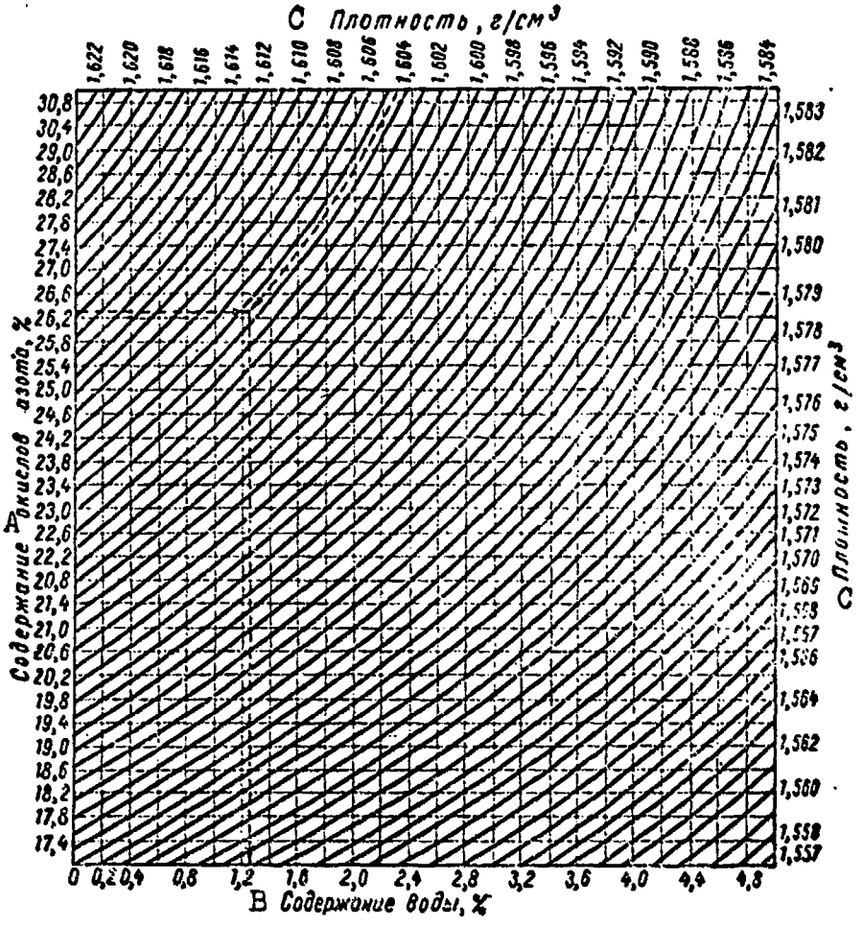


Fig. 278. Density of $HNO_3$-$NO_2$-$H_2O$ system as a function of nitrogen-oxide and water contents at 20°. A) Content of oxides of nitrogen, %; B) water content, %; C) density, g/cm$^3$.

system's vapor pressure due to the reduced solubility of the nitrogen oxides in the diluted nitric acid. Addition of water to such an oxidizer results in vigorous evolution of nitrogen oxides and sharp heating of the product.

The nitrogen oxides in concentrated nitric acid containing small quantities of water are chemically bound with the nitric acid, forming associated molecules corresponding to the formula $NO_2 \cdot 2HNO_3$ [6, 38]. This may account for the fact that the vapor pressure is smaller and the density higher in solutions of nitrogen tetroxide in nitric acid than would be expected on the basis of the laws of Raoult, van't

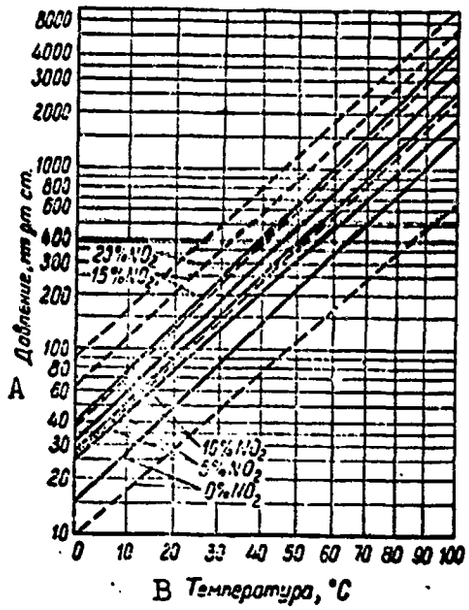


Fig. 279. Vapor pressure of $HNO_3$-$NO_2$-$H_2O$ system as a function of temperature. ——— 0% $H_2O$; – – – 10% $H_2O$. A) Pressure, mm Hg; B) temperature, °C.

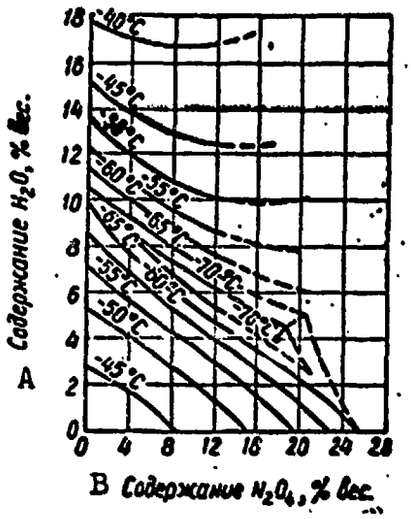


Fig. 280. Freezing-point curves of $HNO_3$-$N_2O_4$-$H_2O$ system. A) $H_2O$ content, % by weight; B) $N_2O_4$ content, % by weight.

Hoff and others for ideal solutions.

Dissolving nitrogen tetroxide in nitric acid makes it possible to produce an oxidizer with a low freezing point (below –60°) (Fig. 280) [37].

The system containing about 17% of nitrogen tetroxide and 4% of water has the lowest freezing point (–78°).

One of the substantial shortcomings of concentrated nitric acid as an oxidizer is its thermal instability. Even at normal temperatures (20-50°), it decomposes into nitrogen tetroxide, water and gaseous oxygen. As a result of accumulation of oxygen in the vapor phase of the oxidizer, large excess pressures (tens of atmospheres) may be set up in a hermetically sealed tank during storage.

The decomposition rate of nitric acid depends on its content of water and nitrogen oxides, as well as on temperature.

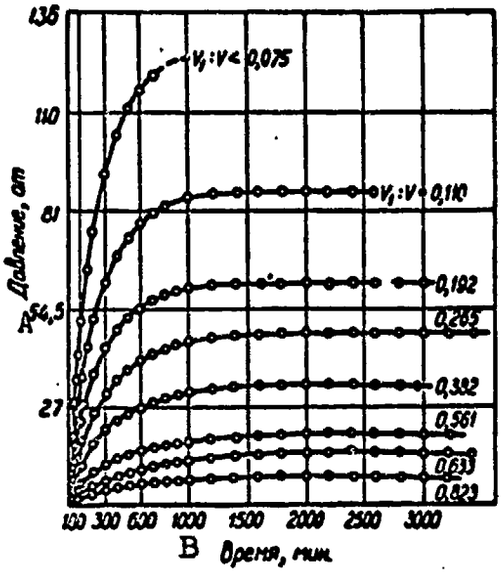


Fig. 281. Decomposition kinetics of 100% nitric acid at 76° and various ratios between the volumes of the vapor ($V_1$) and liquid (V) phases. A) Pressure, atmospheres; B) time, minutes.

The decomposition kinetics of 100% nitric acid at a temperature of 76° and various ratios between the volumes of the vapor and liquid phases is shown in Fig. 281 [39].

The decomposition rate of 96% nitric acid as a function of temperature is shown in Fig. 282.

With increasing content of nitrogen oxides and water in the acid, the rate of its decomposition drops off. To improve the thermal stability of concentrated nitric acid, 16-20% of nitrogen tetroxide is added to it. Oxidizers based on nitric acid that contain about 20% of nitrogen tetroxide are stable in storage for all practical purposes. It is not advisable to raise the stability of nitric acid by water dilution, since the energy properties of the oxidizer deteriorate sharply when this is done.

One of the most important shortcomings of oxidizers based on nitric acid is their aggressive action on metals and nonmetallic materials. Countering corrosion of the metals is one of the major problems encountered in storage and use of nitric-acid-based oxidizers. Almost all metals, with the exception of gold and platinum, corrode to a greater or lesser degree in concentrated nitric acid. Here the following chemical reaction takes place:

$$M+2n\,HNO_3 \rightarrow n\,NO_2+n\,H_2O+M(NO_3)_n,$$

where M stands for a metal that has a valence of n in its oxidized state.

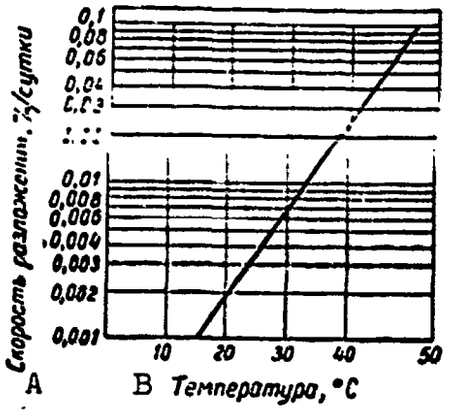


Fig. 282. Decomposition rate of 96% nitric acid as a function of temperature. A) Rate of decomposition, %/day; B) temperature, °C.

The chemically most stable metals used in rocket engineering are aluminum and its alloys, high-silicon iron, and certain grades of stainless steel such as the chromium and chromium-nickel steels [37]. Ordinary low-carbon steel and copper, brass, bronze, lead and the like undergo rapid deterioration under exposure to oxidizers based on nitric acid.

An undesirable factor in operations with inhibited nitric acid and the most usually accompanied corrosion, is the formation of sediment during storage of the oxidizers in aluminum and steel tanks or rocket tanks. While they are first gelatinous in nature, these sediments then condense and become solid grains [6].

The corrosion rate rises significantly with increasing temperature. The corrosion rate of aluminum and stainless steels in oxidizers based on nitric acid is ten times higher at 50° than at a moderate temperature (15-20°).

Various inhibitors are introduced to reduce corrosion of metals in oxidizers based on nitric acid [35]. For example, hydrofluoric acid (HF) added to nitric acid in a quantity of 0.4-0.6% (by weight) lowers the corrosion rate of aluminum and stainless steels in both the vapor and liquid phases by a factor of several hundred [37]. The inhibiting action of hydrofluoric acid is accounted for in terms of formation of a protective fluoride film on the metal's surface.

Orthophosphoric and sulfuric acids are also employed as corrosion inhibitors. The addition of about 1% of orthophosphoric acid to nitric

acid containing 16% of nitrogen tetroxide reduces the corrosion of SAE-1020 steel by a factor of approximately 10 [40].

Concentrated nitric acid mixed with 10% of sulfuric acid, which is known to the engineer as melange, can be stored and shipped in ordinary steel tank cars. The addition of sulfuric to nitric acid improves the oxidizer's ignition properties but is detrimental to its energy characteristics.

A shortcoming of concentrated nitric acid is its strongly manifested hygroscopicity. Dilute nitric acid is characterized by higher chemical activity toward metals than is the concentrated acid. This factor must be taken into account in operations with the oxidizers. If the storage or rocket tanks holding the concentrated nitric acid are not sufficiently airtight, particularly at points where there are threaded and flanged connections, the oxidizer vapor forms the dilute acid with moisture of the air and this, condensing on the metal surface, causes intensive corrosion. A similar effect may also be observed at points of seepage and sweating of the nitric acid.

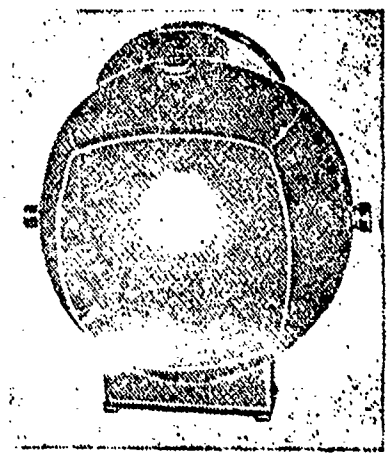

Fig. 283. Spherical tank for storage and shipment of red fuming nitric acid.

Oxidizers based on nitric acid attack the majority of nonmetallic materials: wood, fabrics, cardboard, rubber, most plastics, and so forth. Fluoroplasts, woven glass, ceramics, and various lubricants based on fluorinated hydrocarbons are stable in them for practical purposes.

Nitric-acid-base oxidizers are stored and transported in special containers (tanks, tank cars, drums) made from aluminum or aluminum alloys or from stainless steel [35, 37]. Underground and half-buried storage facilities are used in the USA. with each reservoir

fitted with its own pumping facilities, plumbing and other necessary equipment [35].

Special spherical aluminum tanks with a capacity of 1440 liters and weighing 1800 kg are produced for storage and shipment of red fuming nitric acid in the USA; these are designed for a working pressure of 14 atmospheres (Fig. 283) [41, 42].

Oxidizers based on nitric acid may also be stored in ordinary steel reservoirs that have been inside-coated with fluoroplast or some other chemically stable material [35].

Nitric-acid-base oxidizers are exceedingly aggressive products whose handling requires observance of special precautionary measures. Protective clothing is worn for work with the oxidizers – coveralls or aprons, rubber boots and gloves, gas masks or protective goggles, and so forth. The most reliable protection is afforded by clothing made from glass fabric that has been impregnated with an acid-resistant plastic of the teflon type. Clothing made from polyethylene or Steklovinit cloth may also be used [35].

Serious attention must be given to fire-prevention measures in storage of nitric-acid-base oxidizers, since on coming into contact with combustible materials, these oxidizers may ignite them.

Oxides of Nitrogen

Apart from nitric acid, the oxygen compounds of nitrogen also include nitrogen pentoxide or nitric anhydride, nitrogen tetroxide, nitrogen trioxide or nitrous anhydride, nitric oxide and nitrous oxide, which is also known as "laughing gas."

The physicochemical properties of nitrogen oxides are given in Table 206.

All oxides of nitrogen with the exception of $N_2O$ are more effective as regards energy properties than nitric acid, whose heating

TABLE 206

Physicochemical Properties of Nitrogen Oxides [30, 43]

| 1 Окислы | 2 Химическая формула | 3 Молекулярный вес | 4 Плотность, г/см³ | 5 Температура замерзания, °С | 6 Температура кипения, °С | 7 Теплота образования, ккал/моль | 8 Теплопроизводительность с толуолом, ккал/кг |
|---|---|---|---|---|---|---|---|
| 9 Пятиокись азота | $N_2O_5$ | 108 | 1,64 (20°) | 10 Возг. при 32 | 11 Разлагается | — | 1830 |
| 12 Четырехокись азота | $N_2O_4$ | 92 | 1,45 (20°) | —11,2 | 21,2 | —3,1 | 1790 |
| 13 Трехокись азота | $N_2O_3$ | 62 | 1,45 (2°) | —102 | 4 | 20,0 | — |
| 14 Окись азота . . . . | NO | 30 | 1,27 (—152°) | —164 | —152 | —21,5 | 1610 |
| 15 Закись азота . . . . | $N_2O$ | 44 | 1,23 (—88,5°) | —102 | —88,5 | —19,5 | 1310 |

1) Oxide; 2) chemical formula; 3) molecular weight; 4) density, g/cm$^3$ 5) freezing point, °C; 6) boiling point, °C; 7) heat of formation, kcal/mole; 8) heating value with toluene, kcal/kg; 9) nitrogen pentoxide; 10) sublimates at 32; 11) decomposes; 12) nitrogen tetroxide; 13) nitrogen trioxide; 14) nitric oxide; 15) nitrous oxide.

value with toluene is 1470 kcal/kg.

As regards energy properties, nitrogen pentoxide is most effective as an oxidizer. However, it has not come into practical use because of its thermal instability. Even at normal temperatures, nitrogen pentoxide decomposes rapidly into nitrogen tetroxide and gaseous oxygen:

$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2} O_2.$$

Of all of the above oxides, nitrogen tetroxide is of the greatest practical interest. It is a stable product whose effectiveness is inferior only to that of nitrogen pentoxide.

Nitrogen tetroxide in pure form has not yet come into extensive use in rocket engineering because of the narrow temperature range in which it exists in liquid form at atmospheric pressure (—11.2° to + 21.2°).

Nitrogen tetroxide is mixed with nitric oxide to depress its freezing point. The mixture consisting of 70% $N_2O_4$ and 30% NO freezes

at –80° [36].

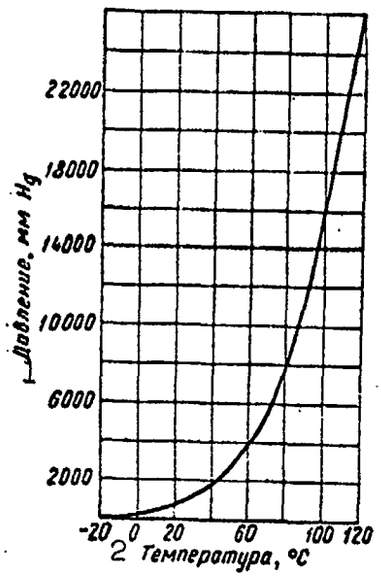


Fig. 284. Vapor pressure of nitrogen tetroxide as a function of temperature. 1) Pressure, mm Hg; 2) temperature, °C.

As regards its energy properties, such a mixture yields nothing to pure nitrogen tetroxide.

A deficiency of the mixture is its low boiling point (–20°). At 20°, the vapor pressure of such an oxidizer reaches 6 atmospheres [36].

At normal temperature, nitrogen tetroxide is a pale yellow liquid whose color turns to brown as the temperature is raised. This takes place as a result of dissociation of the nitrogen tetroxide in accordance with the equation

$$N_2O_4 \rightleftarrows 2NO_2.$$

Nitrogen tetroxide is approximately 20% dissociated at 25°, 40% at 50°, and completely dissociated at 150°.

As a result of dissociation of nitrogen tetroxide, its vapor pressure rises sharply as the temperature is elevated (Fig. 284).

Nitrogen tetroxide is readily soluble in concentrated nitric acid, tetranitromethane and certain organic substances: carbon disulfide, aromatic hydrocarbons, naphthenes, and liquid paraffins, with which it forms stable solutions. Unsaturated hydrocarbons, alcohols, amines and a number of other classes of organic compounds react energetically with nitrogen tetroxide, frequently bursting into flame. It reacts with water in accordance with the equation

$$N_2O_4+H_2O=HNO_3+HNO_2.$$

With regard to metals, pure nitrogen tetroxide is considerably less active than concentrated nitric acid. $N_2O_4$ is stored and shipped

in steel bottles. Aluminum and steel tank cars and drums may also be used for these purposes [6, 4].

TETRANITROMETHANE

Tetranitromethane $C(NO_2)_4$, whose molecule contains a large quantity of active oxygen, is a promising oxidizer, and more effective than concentrated nitric acid.

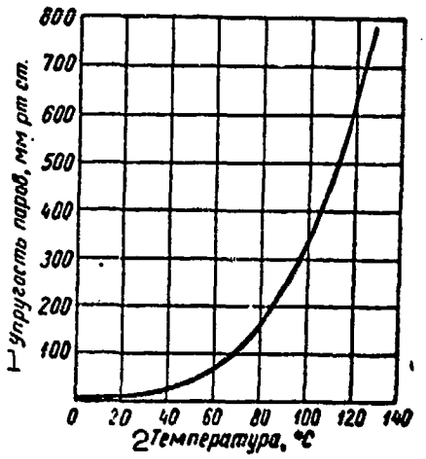


Fig. 285. Vapor pressure of tetranitromethane as a function of temperature. 1) Vapor pressure, mm Hg; 2) temperature, °C.

Tetranitromethane is produced by nitration of acetylene with nitric acid [45]. The reaction takes place in accordance with the following over-all equation:

$$5HC{=}CH+38HNO_3 \rightarrow C(NO_2)_4+7CO_2+26O_2+24H_2O.$$

Tetranitromethane is a heavy mobile liquid with a faint green coloration and a sharp odor. Pure tetranitromethane has a density of 1.643 at a temperature of 20°, boils at 125° and freezes at +13.8° [6].

The dependence of its vapor pressure on temperature is shown in Fig. 285.

The heat of formation of tetranitromethane is 8.9 kcal [46].

Its viscosity at 15° is 0.0165 poise.

At normal temperature, tetranitromethane is a stable substance and can be stored for years without undergoing any noticeable changes. Only when heated above 100° does it undergo partial decomposition with formation of nitrogen oxides and carbon dioxide. It has very low solubility in water. It is stable in acid and neutral media. Tetranitromethane reacts with alkalis to form explosive nitroform salts [6]. Tetranitromethane is itself a low explosive. Its mixtures with hydrocarbons are highly explosive [45]. An important advantage of tetranitromethane over nitric acid is its low corrosive activity with re-

spect to structural metals and alloys.

Glass, stainless steel, aluminum and lead do not corrode in tetranitromethane. Iron, copper, and even polyvinyl chloride react readily with it. Brass, zinc, rubber and polyisobutylene deteriorate markedly in contact with tetranitromethane [45].

An essential disadvantage of tetranitromethane, and one that represents an obstacle to its use in pure form, is its high freezing point (+13.8°). In view of this, it is recommended that tetranitromethane be used after mixing with nitrogen tetroxide. A mixture consisting of 70% tetranitromethane and 30% nitrogen tetroxide freezes at a temperature below −25° [47]. Here, the oxidizer's energy properties remain practically the same as those of pure tetranitromethane.

Tetranitromethane is poisonous and severely irritates the mucous membranes of the eye, nose, and respiratory tract. Symptoms of chronic tetranitromethane poisoning include persistent headaches, fatigue, languor and bradycardia.

Prolonged exposure of the organism to tetranitromethane gives rise to nervous disorders and impaired cardiac activity [45].

## FLUORINE AND FLUORINE COMPOUNDS

Liquid fluorine and certain of its compounds – fluorine monoxide, chlorine trifluoride, nitroxyfluoride, bromine pentafluoride, nitrogen trifluoride, tetrafluorohydrazine, and others – are worthy of attention as promising oxidizers [1, 2, 36, 53].

The physical parameters of fluorine and some of its derivatives are listed in Table 207.

The basic energy characteristics of fuels based on liquid fluorine and some of its derivatives are listed in Table 208.

### Liquid Fluorine

Fluorine is one of the most reactive chemical elements. The high

TABLE 207

Physical Parameters of Fluorine and its Derivatives [6, 9]

| 1 Окислители | 2 Химическая формула | 3 Молекулярный вес | 4 Плотность, г/см³ | 5 Температура застывания, °С | 6 Температура кипения, °С | 7 Теплопроизводительность с водородом, ккал/кг |
|---|---|---|---|---|---|---|
| 8 Фтор . . . . . | $F_2$ | 38,00 | 1,11 (—187°) | —223,0 | —187,0 | 3120 |
| 9 Монооксид фтора | $OF_2$ | 54,00 | 1,53 (—144°) | —223,8 | —144,8 | 3270 |
| 10 Перекись фтора . . | $O_2F_2$ | 70,00 | 1,45 (—57°) | —163,5 | —57,0 | 3130 |
| 11 Трифторид хлора | $ClF_3$ | 92,46 | 1,77 | —82,6 | +12,1 | 2160 |
| 12 Нитроксифторид . . | $FNO_3$ | 81,00 | 1,51 (—46) | —176,0 | —45,9 | 2640 |
| 13 Трехфтористый азот | $NF_3$ | 71,00 | 1,92 (—208) | —208,5 | —129,0 | 2240 |
| 14 Пятифтористый бром | $BrF_5$ | 174,96 | 2,47 (20) | —61,3 | +40,5 | 1780 |

1) Oxidizer; 2) chemical formula; 3) molecular weight; 4) density, g/cm$^3$; 5) freezing point, °C; 6) boiling point, °C; 7) heating value with hydrogen; kcal/kg; 8) fluorine; 9) fluorine monoxide; 10) fluorine peroxide; 11) chlorine trifluoride; 12) nitroxyfluoride; 13) nitrogen trifluoride; 14) bromine pentafluoride.

potential of fluorine as an oxidizer has long attracted the attention of investigators [6].

The ZhRD fuels presently in widespread use make possible specific thrusts of only about 230-280 kg·sec/kg with a 35-atmosphere combustion-chamber pressure [48]. Liquid fluorine is the most powerful of all known oxidizers. In combination with such combustibles as hydrazine or ammonia, it delivers a specific thrust of about 305-316 kg·sec/kg at a chamber pressure of 25 kg/cm$^2$, or 373 kg·sec/kg with liquid hydrogen [48, 49].

Under normal conditions, free fluorine is a greenish-yellow gas with a sharp unpleasant odor. Liquid fluorine is yellow in color. Its viscosity at the boiling point is 2.75 centipoises, and the latent heat of evaporation is 1.58 kcal/mole.

The chemical properties of fluorine are determined by its high affinity to the electron. All reactions with fluorine take place by donation of electrons from atoms of other elements, i.e., the fluorine

TABLE 208

Energy Characteristics of Fuels Based on Liquid Fluorine and Certain of its Derivatives [5]

| 1 Топливная смесь | 2 Отношение окислителя к горючему | 3 Плотность топлива, кг/л | 4 Температура в камере сгорания, °С | 5 Удельная тяга, кг сек/кг |
|---|---|---|---|---|
| 6 Фтор + водород | 9,42 | 0,46 | 4480 | 380 |
| 7 Фтор + водород | 3,8 | 0,27 | 2540 | 360 |
| 8 Фтор + гидразин | 2 | 1,3 | 4260 | 280 |
| 9 Фтор + аммиак | 3 | 1,16 | 4020 | 300 |
| 10 Фтор + диборан | 5 | 1,07 | 4360 | 255 |
| 11 Фтор + топливо JP-4 | 2,9 | 1,19 | 3980 | 275 |
| 12 Монооксид фтора + аммиак | 1,9 | 1,07 | 3340 | 260 |
| 13 Монооксид фтора + гидразин | 1,1 | 1,23 | 3525 | 257 |
| 14 Трифторид хлора + аммиак | 3 | 1,26 | 2750 | 238 |
| 15 Трифторид хлора + гидразин | 2,5 | 1,46 | 3815 | 247 |
| 16 Пентафторид брома + аммиак | 6 | 1,8 | 3680 | 245 |
| 17 Фтор (50%) и трифторид азота (50%) + аммиак | 2,8 | 1,15 | 3615 | 290 |

Note. The combustion-chamber pressure is assumed equal to 28 kg/cm$^2$.

1) Fuel mixture; 2) oxidizer-to-combustible ratio; 3) density of fuel, kg/liter; 4) temperature in combustion chamber, °C; 5) specific thrust, kg·sec/kg; 6) fluorine + hydrogen; 7) fluorine + hydrogen; 8) fluorine + hydrazine; 9) fluorine + ammonia; 10) fluorine + diborane; 11) fluorine + JP-4 fuel; 12) fluorine monoxide + ammonia; 13) fluorine monoxide + hydrazine; 14) chlorine trifluoride + ammonia; 15) chlorine trifluoride + hydrazine; 16) bromine pentafluoride + ammonia; 17) fluorine (50%) and nitrogen trifluoride (50%) + ammonia.

is always the oxidizer. Even at ordinary temperatures, it reacts vigorously with almost all organic and inorganic substances, and the reactions are accompanied by evolution of a large quantity of heat and frequently a flame. Chlorine burns in a fluorine atmosphere. Hydrocarbons burn in fluorine just as they would in oxygen. Inert gases, fluorides of heavy metals, fluoroplasts and such elements as bismuth, zinc, tin, lead, gold and platinum do not react or react only insignificantly with fluorine. Copper, chromium, manganese, nickel, monel metal, stainless steel and aluminum are practically stable in contact with fluorine when water is absent, due to the formation of a tough

protective film of the corresponding fluoride on their surfaces. At elevated temperatures, nickel and its alloys, as well as stainless steel, show satisfactory stability [6].

Fluorine reacts with water to form hydrogen fluoride and oxygen, as well as small quantities of ozone, hydrogen peroxide and fluorine monoxide. In the presence of a spark, fluorine reacts explosively with atmospheric moisture.

Before the Second World War, elementary fluorine had been produced only in small quantities for laboratory purposes. The development of research in atomic energy necessitated creation of a large capacity for production of the fluorine needed to produce uranium hexafluoride [50].

Liquid fluorine is now produced industrially in large quantities [51]. The element has a broad raw-material base. Its total content in the Earth's crust is 0.02%. The basic natural starting material for the production of fluorine is fluorspar ($CaF_2$) [49].

One of the basic shortcomings of liquid fluorine, as in the case of liquid oxygen, is its low boiling point ($-187^{\circ}$). Under normal conditions, it evaporates continuously and contaminates the atmosphere with poisonous fumes. It has been necessary to develop special apparatus for the storage and shipment of liquid fluorine, and to take special precautionary measures in work with it.

Gaseous fluorine is stored and transported in seamless bottles under high pressure. For the storage of liquid fluorine in the USA, for example, special reservoirs made from stainless steel or aluminum have been developed [51]. They consist of three horizontal reservoirs inserted one inside another. The first (internal) reservoir is filled with liquid fluorine. The space between the walls of the first and second reservoirs is filled with liquid nitrogen, whose boiling point

is 14° lower than that of fluorine. This circumstance makes it possible to store liquid fluorine under a light vacuum and prevent it from leaking into the atmosphere. A heat-insulating material is placed between the walls of the second and third reservoirs. Reservoirs for shipment of liquid fluorine are similarly constructed; these are carried on special truck trailers or railroad platform cars.

At the present time, liquid fluorine in large quantities is shipped in special tank trucks in the USA [18]. Transfer of the liquid fluorine to the customer's capacity is accomplished by setting up an excess pressure ir the reservoir with helium or by preheating the fluorine in a special tubing system.

A negative property of fluorine is its high toxicity. It has a destructive effect on the mucous membranes of the eyes, nose and respiratory tract, as well as on the integument. Even brief residence in a fluorine atmosphere may have a fatal outcome. The admissible concentration of fluorine vapor in air is 0.001 mg/liter [20]. Placing a finger or hand into an atmosphere of pure fluorine results in the formation of lesions.

Neoprene jackets, trousers, boots and gloves are used to protect the skin from fluorine, and a closed-circuit gas mask to protect the respiratory organs and the eyes. It is recommended that goggles have metallic frames, since plastic frames may ignite in a fluorine atmosphere [6]. Liquid fluorine may be neutralized with bicarbonate of soda or a solution of calcined soda [18]. Use of water to extinguish fires that have broken out as a result of contact between fluorine and organic materials is not recommended, since the fluorine reacts with it vigorously to form toxic hydrogen fluoride.

Fluorine Derivatives

Among the fluorine derivatives, the most effective oxidizer is

fluorine monoxide ($OF_2$). Its advantages over fluorine consist in a higher boiling point (–144.8°) and a higher specific gravity (1.5), while exceptionally high toxicity is a drawback. The admissible concentration of fluorine monoxide vapor in air is 0.00001 mg/liter [20]. At the temperature of liquid air, fluorine monoxide is a yellow liquid with brownish overtones. As compared with fluorine, the monoxide is distinguished by lower chemical activity as a result of a higher activation energy of decomposition. Self-ignition does not occur when fluorine monoxide is mixed with hydrogen, methane and other organic substances [9]. Concentrated alkali solutions decompose it.

Fluorine monoxide can be prepared by passing fluorine through a 27% solution of alkali by the reaction [6, 9]

$$2F_2+2NaOH \rightarrow OF_2+2NaF+H_2O.$$

Chlorine Trifluoride

Chlorine trifluoride is a promising oxidizing agent. It delivers approximately the same potential specific thrust as nitrogen tetroxide.

Chlorine trifluoride is most effective when used in combination with combustibles based on amines or hydrazines. It is less effective with hydrocarbon combustibles [36].

Under normal conditions, chlorine trifluoride is a light green gas.

Liquid chlorine trifluoride is characterized by a comparatively high boiling point (+11.3°), a low freezing point (–76.3°), a high density (1.85 at the boiling point) and satisfactory energy properties. These facts, together with the possibility of storing it in tanks made of ordinary steel, enable us to regard chlorine trifluoride as a promising oxidizer [52, 53]. It is produced as a result of reaction of fluorine with chlorine in a mixture with nitrogen in a copper or nickel reactor at a temperature of 280°, with subsequent cooling of

the gas mixture to $-70^{\circ}$ [9].

Chlorine trifluoride is produced on an industrial scale. As regards its chemical properties, chlorine trifluoride is an extremely reactive substance. Many organic substances ignite spontaneously on contact with it, as does glass wool. It reacts explosively with water.

Nitroxyfluoride (Fluorine Nitrate)

Nitroxyfluoride is known as one of the most powerful oxidizers [6]. Under normal conditions, it is a colorless gas with a characteristic pungent odor and possesses high toxicity. It is produced in the reaction of fluorine with concentrated nitric acid in accordance with the equation [54]

$$HNO_3 + F_2 \rightarrow FNO_3 + HF.$$

Liquid nitroxyfluoride has a density 1.5 times that of liquid oxygen. The use of nitroxyfluoride as an oxidizer in pure form is rendered difficult by the fact that it possesses explosive properties [54, 55].

Bromine pentafluoride also merits attention as an oxidizer; under normal conditions, this is a liquid that boils at $+40.5^{\circ}$ and freezes at $-61.3^{\circ}$. This is one of the heaviest oxidizers. Its specific gravity at a temperature of $20^{\circ}$ is 2.47 [9]. Bromine pentafluoride is an extremely stable substance that does not decompose even at $460^{\circ}$. Bromine pentafluoride is an effective oxidizer, as is chlorine trifluoride [5, 53].

PERCHLORIC ACID AND CHLORINE OXIDES

Oxygen compounds of chlorine, which are characterized by high chemical activity, may be employed as oxidizers for ZhRD [9]. Anhydrous perchloric acid ($HClO_4$) and chlorine heptoxide ($Cl_2O_7$) are of practical interest. The salts of perchloric acid (chlorates and per-

chlorates) have come into use as oxidizing components in solid rocket fuels [56].

Chemically pure perchloric acid is a colorless liquid that fumes in air, has a density of 1.77, and freezes at a temperature of $-112^{\circ}$. The low freezing point, high density and high effectiveness make this oxidizer highly attractive for applications in rocket engineering. The boiling point of perchloric acid is $110^{\circ}$. On heating above $90^{\circ}$, however, the acid decomposes violently. Complete decomposition of perchloric acid takes place with evolution of heat, in accordance with the equation

$$HClO_4 \rightarrow \frac{1}{2}H_2O + \frac{1}{2}Cl_2 + 1{,}75\ O_2 + 15{,}7\text{kcal}.$$

Perchloric acid that has been subject to partial decomposition is colored from dark red to brownish. Unlike chlorine oxides, pure perchloric acid has no explosive properties. However, addition of small quantities (3%) of organic substances to it results in formation of a highly explosive mixture [9]. Partially decomposed perchloric acid explodes as a result of accumulation of chlorine dioxide, which has strong explosive properties. When perchloric acid is stored, it decomposes in accordance with the equation

$$3HClO_4 \rightleftarrows Cl_2O_7 + H_2O \cdot HClO_4,$$

$$Cl_2O_7 \rightarrow 2ClO_2 + 1\frac{1}{2}O_2.$$

The decomposition of perchloric acid, which is autocatalytic in nature, is one of its most important shortcomings. Another important deficiency of perchloric acid is its strongly manifested hygroscopicity, which leads to the formation of hydrates and, as a result, a sharp rise in the freezing point. Addition of one molecule of water to the perchloric-acid molecule ($HClO_4 \cdot H_2O$) raises the freezing point of the acid from $-112^{\circ}$ to $50^{\circ}$, i.e., by $162^{\circ}$. This is accompanied by a sharp increase in the viscosity of the perchloric acid.

Organic substances (amines, unsaturated hydrocarbons, rubber, paper, cloth, wood and others) self-ignite, sometimes explosively, on contact with perchloric acid. On striking the skin, it produces deep painful burns. Aluminum and stainless steel are quite stable in perchloric acid. Iron and ordinary steels corrode rapidly in it.

At normal temperatures, chlorine heptoxide is a heavy colorless oil that freezes at a temperature of $-83.1^{\circ}$ and boils at $80.1^{\circ}$ [6]. Its density is approximately the same as that of perchloric acid. In storage, chlorine heptoxide undergoes noticeable decomposition. Like other oxygen compounds of chlorine, it has a tendency to explode under certain conditions. Organic materials (wood, paper, and so forth) self-ignite on contact with chlorine heptoxide. It reacts with water to form perchloric acid. Despite its essential shortcomings, chlorine heptoxide is of interest as an oxidizer. Calculations indicate that a mixture of chlorine heptoxide (85%) and nitrogen tetroxide (15%) is a more effective oxidizer than nitric acid containing 22% of nitrogen tetroxide [5].

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858 кр = kr = kriticheskiy = critical

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## Chapter 27

## MONOPROPELLANTS FOR LIQUID ENGINES

Monopropellants consist of substances whose molecules contain (in their composition) combustible elements and the required oxygen for combustion, as well as stable mixtures (solutions) of combustibles and oxidizers that do not enter into chemical reactions with one another at standard temperatures. Such propellants do not require the supply of an oxidizer into the combustion chamber during combustion.

Monopropellants also include the endothermic compounds which liberate a great quantity of heat and gaseous products as they decompose.

The advantage of monopropellants over bipropellants lies in the possibility of simplifying the feed systems and in the related possibility of reducing engine weight, since the utilization of monopropellants eliminates the need for a second fuel tank, a pump, for devices to mix the fuel components in the combustion chamber, etc.

The danger of explosion and the comparatively low heat of combustion are significant shortcomings which stand in the way of the extensive utilization of monopropellants in ZhRD (liquid engines). With a combustible-oxidizer ratio equal to or close to the stoichiometric, monopropellants tend to detonation under the action of friction, impact, heating, or similar factors. In order to reduce the danger of explosion it becomes necessary to design systems exhibiting a negative oxygen balance, and this results in incomplete combustion, which, in turn, has as its consequence a reduction in the heat of combustion of the propellant.

Monopropellants are individual compounds or homogeneous mixtures that are characterized by a constancy of the basic characteristics (heats of combustion, the excess oxidizer ratio, the burning rate, etc.), determined by the composition of the propellant.

At the present time monopropellants are used primarily as auxiliary fuels (propellants).

To start engines operating on monopropellants a special ignition system is required.

MONOPROPELLANTS OF MOLECULAR COMPOSITION

The liquids containing chemically combined oxygen in their molecules in quantities adequate to provide for normal combustion are included in this class of propellants.

The esters of nitric acid and various mon-, bi-, and triatomic alcohols (methyl nitrate, diethyleneglycol dinitrate, trinitroglycerine), liquid nitroparaffins (nitromethane, nitropropane), etc., can be used as such propellants [1, 2].

The physicochemical properties of certain nitro esters and the lower nitroparaffins are presented in Tables 209 and 210 [1, 3].

Of the nitro-esters presented in Table 209 glycerine trinitrate, ethyleneglycol dinitrate, and methyl nitrate are particularly noteworthy in terms of the magnitude of the heat of combustion and in terms of density. All three compounds are readily accessible. They are derived by the nitration of the corresponding alcohols with a mixture of concentrated nitric and sulfuric acids.

In pure form and at normal temperatures these compounds are quite stable. However, they exhibit a great tendency to detonation, and this is brought about by the high oxygen content in their molecules. In the ethyleneglycol-dinitrate molecule the quantity of oxygen corresponds to the stoichiometric, and in the glycerine-trinitrate molecule the

quantity of oxygen is even higher than the stoichiometric. Such compounds may be made to explode as a result of a shock, friction, a pronounced increase in temperature and pressure, contamination, and similar factors. As a result they are dangerous to handle and little suited for utilization as propellants for liquid engines.

No effective means have as yet been found to suppress detonation without impairing the basic properties of these propellants.

To reduce the danger of explosion from these monopropellants, they may be employed in a mixture with inert and explosion-safe substances that do not contain oxygen, or contain oxygen in small quantities. We know, for example, of the use of a mixture consisting of 70% methyl nitrate and 30% methyl alcohol [1]. The utilization of similar mixtures provides for more uniform propellant combustion, but the completeness of combustion in this case diminishes as a result of a lack of oxygen to oxidize the combustible elements of the actual propellant and the solvent.

The dilution of methyl nitrate with 30% methyl alcohol reduces the heat of combustion to 740 kcal/kg, i.e., by a factor of almost two in comparison with pure nitro esters. In terms of the heat of combustion such a mixture corresponds virtually to pure ethyl nitrate (see Table 209), and this indicates the fact that there is little point in using such mixtures, especially when we consider the fact that they are not completely safe.

In the USA a mixture of ethyl nitrate with propyl nitrate (specification MIL-E-26603) is used as a nitro-ester monopropellant in auxiliary liquid engines, as is pure propyl nitrate (specification MIL-R-25576).

Of the nitrogen compounds, nitromethane is of practical interest as a monopropellant (see Table 210). The nitroparaffins are obtained

TABLE 209

Physicochemical Properties of Certain Nitric-Acid Esters

| 1 Эфиры | 2 Химическая формула | 3 Мол. вес | 4 Плотность при 20°, г/см³ | 5 Температура кипения, °С | 6 Кислородный баланс в % к стехиометрическому | 7 Теплота сгорания за счет собственного кислорода, ккал/кг | 8 Чувствительность к удару (высота падения 2 кг груза), см |
|---|---|---|---|---|---|---|---|
| 9 Метилнитрат | $CH_3ONO_2$ | 77 | 1,21 | 65 | 85,71 | 1490 | 40 |
| 10 Этилнитрат | $C_2H_5ONO_2$ | 91 | 1,12 | 87 | 46,15 | 713 | — |
| 11 Пропилнитрат | $n$-$C_3H_7ONO_2$ | 105 | 1,06 | 110 | 31,58 | 549 | — |
| 12 Изопропилнитрат | $i$-$C_3H_7ONO_2$ | 105 | 1,02 | 98 | 31,58 | | — |
| 13 Этиленгликольдинитрат | $C_2H_4(ONO_2)_2$ | 152 | 1,50 | 85 (10 мм) | 100,00 | 1581 | 20—25 |
| 14 Этиленгликольмононитрат | $C_2H_4OHONO_2$ | 107 | 1,35 | 92 (10 мм) | 61,54 | 856 | — |
| 15 Пропиленгликольдинитрат | $C_3H_6(ONO_2)_2$ | 166 | 1,37 | 92 (10 мм) | 66,67 | 1109 | — |
| 16 Глицеринтринитрат (тринитроглицерин) | $C_3H_5(ONO_2)_3$ | 227 | 1,60 | 17 Разлагается | 105,8 | 1485 | 4—8 |

1) Esters; 2) chemical formula; 3) molecular weight; 4) density, at 20°, g/cm3; 5) boiling point, °C; 6) oxygen balance in % of stoichiometric; 7) heat of combustion attributable to internal oxygen, kcal/kg; 8) sensitivity to shock (the drop height of a 2-kg weight), in cm; 9) methyl nitrate; 10) ethyl nitrate; 11) propyl nitrate; 12) isopropylnitrate; 13) ethyleneglycol dinitrate; 14) ethyleneglycol mononitrate; 15) propyleneglycol dinitrate; 16) glycerine trinitrate (trinitroglycerine); 17) decomposes.

TABLE 210

The Physicochemical Properties of Certain Nitroparaffins

| 1 Нитропарафины | 2 Мол. вес | 3 Плотность при 20°, г/см³ | 4 Температура, °С: 5 кипения | 6 замерзания | 7 Кислородный баланс в % к стехиометрическому | 8 Теплота сгорания, ккал/кг: 9 за счет собственного кислорода | 10 при сжигании в кислороде | 11 Чувствительность к удару |
|---|---|---|---|---|---|---|---|---|
| 12 Нитрометан $CH_3NO_2$ | 61 | 1,13 | 101 | —29 | 57,14 | 1040 | 2281 | 15 Малочувствителен |
| 13 Нитроэтан $C_2H_5NO_2$ | 76 | 1,05 | 103 | — | 30,77 | 680 | 4340 | 16 Практически нечувствителен |
| 14 1-нитропропан $C_3H_7NO_2$ | 89 | 0,99 | — | — | — | — | 5360 | 17 То же |

1) Nitroparaffins; 2) molecular weight; 3) density, at 20°, g/cm3; 4) temperature, °C; 5) of boiling; 6) of freezing; 7) oxygen balance in % of the stoichiometric; 8) heat of combustion, kcal/kg; 9) attributable to [Key continued on following page]

[Key to Table 210 continued]: internal oxygen; 10) during combustion in oxygen; 11) sensitivity to shock; 12) nitromethane; 13) nitroethane; 14) 1-nitropropane; 15) slightly sensitive; 16) virtually insensitive; 17) the same.

by the nitration of the corresponding hydrocarbons with concentrated nitric acid at elevated temperatures.

Nitromethane is a colorless oily liquid with a boiling point of 101° and a rather low freezing point (-29°). With a negative oxygen balance nitromethane exhibits a relatively high heat of combustion (1040 kcal/kg). The nitromethane exhibits low sensitivity to shock and friction [3, 4], it cannot be detonated by a standard detonator cap or by the firing of a bullet through it, but it will explode if the explosion is initiated by a large trotyl [trinitrotoluene] charge [5]. The addition of small quantities of solvents (gasoline, alcohol) to the nitromethane somewhat reduces its tendency to detonation [6]. In air nitromethane burns quietly with an almost invisible pale flame and without detonation [7].

To improve the completeness of nitromethane combustion in the combustion chamber of an engine, it is recommended that combustion catalysts (salts of chromium, cobalt, nickel, copper, lead, and manganese) be added to the nitromethane [6].

When using nitromethane, its reliable ignition in the engine is of great significance; an ignition lag may result in an explosion.

According to the data of F. Bellindzher [sic] and his coworkers [5, 8] nitromethane as a propellant exhibits the following operational characteristics:

| | |
|---|---|
| Heat of combustion, kcal/kg | 1040 |
| Product-of-combustion exhaust velocity, m/sec | 1780 |
| Temperature of combustion, °C | 2170 |
| Specific engine thrust, kg·sec/kg | 182 |

## MIXTURES OF COMBUSTIBLES AND OXIDIZERS

Monopropellants based on mutually soluble combustibles and oxidizers can be obtained in two ways:

by the selection of a solution of a combustible in an oxidizer of such composition as will burn as a result of the internal oxygen while being, at the same time, explosion-safe; such mixtures generally contain an excess of combustible over the stoichiometric;

by preparing a stoichiometric combustible-oxidizer mixture with the subsequent solution in this mixture of an inert substance (generally water) – not participating in the combustion – to reduce the explosive properties.

As an example of monopropellants obtained by the mutual solution of combustibles and oxidizers we can cite the following mixtures [1, 6]:

concentrated hydrogen peroxide, ethyl or methyl alcohol, and water;

nitrogen tetroxide and benzene or toluene;

tetranitromethane and hydrocarbons or their nitrogen derivatives;

tetranitromethane, ethyl alcohol and water.

Mixtures of combustibles and oxidizers have not yet come into extensive use in liquid engines, although research in this area is continuing. The dominant stress is being laid on seeking methods of improving the stability of propellant mixtures during long storage, as well as on the development of effective phlegmatizer solvents whose use would make it possible to increase the power characteristics of the propellants.

## MONOPROPELLANTS BASED ON ENDOTHERMIC COMPOUNDS

Certain endothermic compounds liberating a great quantity of heat energy and gaseous products of decomposition have found widespread

application as monopropellants. Such compounds include primarily hydrogen peroxide, hydrazine, and ethylene oxide [9-11].

Hydrogen Peroxide

In examining the properties of hydrogen peroxide as an oxidizer it has already been noted that it decomposes easily when heated or in

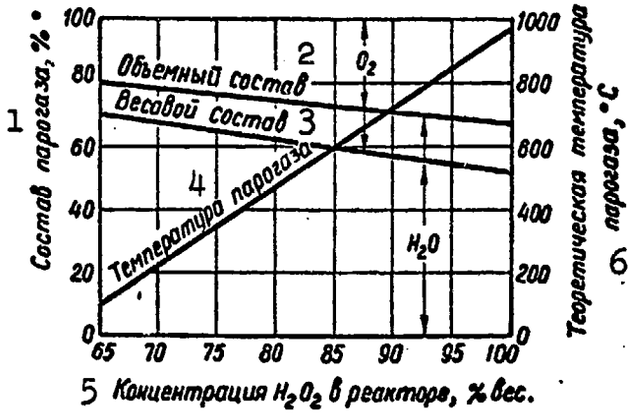


Fig. 286. Composition and temperature of vapor gas derived in the decomposition of various concentrations of hydrogen peroxide. 1) Composition of vapor gas, %; 2) volumetric composition; 3) gravimetric composition; 4) temperature of vapor gas; 5) concentration of $H_2O_2$ in reactor, % by weight; 6) theoretical vapor-gas temperature, °C.

the presence of water- or oxygen-based catalysts. As a result of the decomposition of 1 kg of hydrogen peroxide 690 kcal of heat are liberated, as a result of which the products of decomposition (vapor gas) are heated to 975° and can serve as a source of reaction force. This serves as the basis for the utilization of hydrogen peroxide as a monopropellant.

The decomposition of hydrogen peroxide under the action of various catalysts takes place rather "softly" and at a fast rate.

The temperature of the vapor-gas mixture formed during the decomposition of the hydrogen peroxide is a function of the concentrati

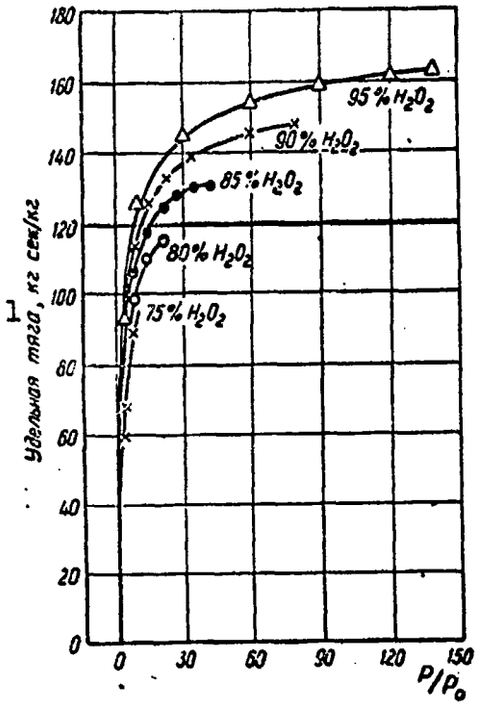


Fig. 287. Specific engine thrust as a function of hydrogen-peroxide concentration and the pressure in the chamber. p) Pressure in chamber; $p_0$) pressure at nozzle outlet; 1) specific thrust, kg·sec/kg.

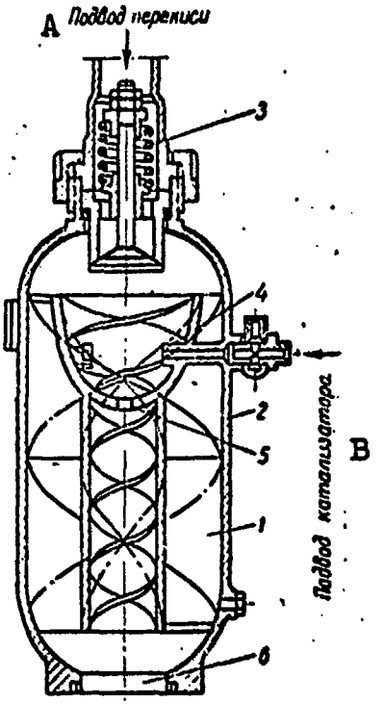


Fig. 288. Diagram of vapor-gas-generator reactor operating with a liquid catalyst. 1) Coil; 2) frame; 3) hydrogen-peroxide injector; 4) catalyst injector; 5) drain orifice; 6) drainage tube for vapor gas; A) peroxide inlet; B) catalyst inlet.

of the latter (Fig. 286). The lower the concentration of the hydrogen peroxide, the greater the water content in the peroxide, and a significant quantity of heat must be expended to vaporize and superheat the vapors of this water.

The low temperature of the vapor-gas mixture that is formed makes it possible to use the reaction of the hydrogen-peroxide decomposition in the gas turbines that are used to actuate the liquid-engine pumps, as well as to design various simple liquid engines of low power that require no cooling (booster engines, helicopter engines, torpedo engines, etc.).

Figure 287 shows the specific thrust of an engine as a functi of the hydrogen-peroxide concentration [6].

To speed up the hydrogen-peroxide-decomposition reaction spec catalysts are employed – pyrolusite (manganese dioxide $MnO_2$), so permanganate $NaMnO_4$, potassium permanganate $KMnO_4$, calcium permanganate $Ca(MnO_4)_2$, sodium bichromate $Na_2Cr_2O_7$, and certain other substances.

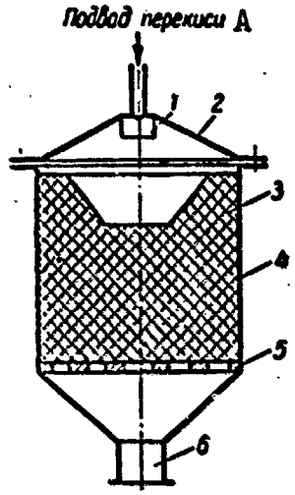


Fig. 289. Diagram of vapor-gas-generator reactor operating on solid catalyst. 1) Injector head; 2) cover plate; 3) catalyst charge; 4) reactor frame; 5) barrier; 6) vapor-gas outlet tube; A) peroxide inlet.

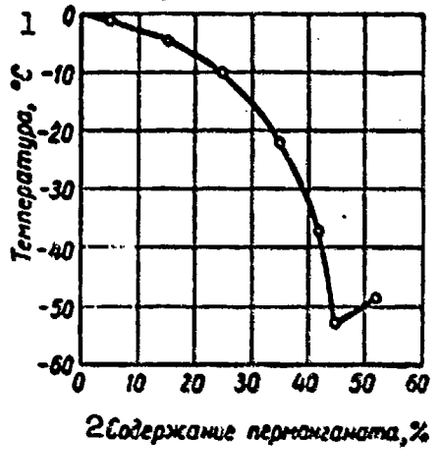


Fig. 290. Freezing point of aqueous solutions of calcium permanganate as a function of its concentration. 1) Temperature, °C; 2) permanganate content, %.

The catalyst may be employed either in the form of an aqueous solution that is injected through a spray nozzle (injector) into the decomposition chamber simultaneously with the hydrogen peroxide, or it may be used in solid form. In the latter case, the ceramic fitting against which the atomized hydrogen peroxide strikes is soaked in the catalyst. One kilogram of solid catalyst can decompose up to 2000

of 80% hydrogen peroxide [12].

Vapor-gas-generator reactors using liquid and solid catalysts are shown in Figs. 288 and 289.

The utilization of solid catalysts is more convenient, since in this form they can be placed into the decomposition chamber in sufficient time, and this simplifies the design of the engine and improves the reliability of engine operation.

Of the liquid catalysts, the 28-32% aqueous solution of sodium permanganate (summer catalyst) and the 37-39% aqueous solution of calcium permanganate (Fig. 290), exhibiting a low freezing point (winter catalyst), are in use. The catalyst consumption amounts to 5-6% of the consumption of 80% hydrogen peroxide [8].

The permanganates are rather powerful oxidizers. In aqueous solutions they easily liberate the oxygen and can ignite many organic materials. When working with permanganates it is extremely important to be very careful.

Hydrazine

Anhydrous hydrazine, as has already been pointed out above, decomposes into gaseous products (nitrogen and ammonia) at elevated temperatures, liberating heat in accordance with the following equation:

$$3N_2H_4 \rightarrow N_2 + 4NH_3.$$

The heat of hydrazine decomposition is comparatively low — 376 kcal/kg. To accelerate the hydrazine-decomposition reaction certain catalysts are employed (oxides of iron, chromium, copper, and so forth).

Hydrazine may be used as a monopropellant for the operation of the turbopump assemblies in ZhRD (liquid [rocket] engines) and in en-

gines of low power [70].

On the basis of the power indicators, hydrazine is not on a pa with concentrated hydrogen peroxide.

Ethylene Oxide ($C_2H_4O$)

In recent years ethylene oxide has been investigated as a monopropellant [13-16]. At the present time it is used in the USA as a propellant (specifications Mil-P-8845 and MPD-574) in auxiliary powerplants of certain large ballistic rockets [16].

Ethylene oxide has found widespread application in industry primarily as the initial product for a number of important syntheses; it is being produced on a sufficiently large industrial scale. Ethylene oxide is produced by the direct oxidation of ethylene [17].

At normal temperatures ethylene oxide is a colorless gas; it has an ether-like odor, and it thickens easily into a clear, highly mobile liquid which exhibits a boiling point of 13.5°. The density of ethylene oxide ($\rho_4^{20}$) is equal to 0.884 and the freezing point is equal to −111.5°. The physical properties of ethylene oxide as functions of temperature are presented in Figs. 291 and 292.

A mixture of ethylene-oxide vapors and air can be ignited by heating or by a spark in a wide range of concentrations – from 3 to 80%.

When heated in the presence of catalysts, ethylene oxide decomposes and liberates gaseous products of decomposition as well as heat. In terms of heat of decomposition (726 kcal/kg) ethylene oxide corresponds approximately to powders. The theoretical decomposition of ethylene oxide can be presented in the following form:

$$CH_2-CH_2 \rightarrow CO+CH_4+q.$$

The actual decomposition of ethylene oxide takes place in accor-

with the following equation [6]:

$$CH_2-CH_2 \rightarrow a\,CO + b\,CH_4 + c\,C_2H_4 + d\,H_2.$$

The formation of side products of decomposition $C_2H_4$ and $H_2$ reduces the thermal effect of the reaction. The percentage composition

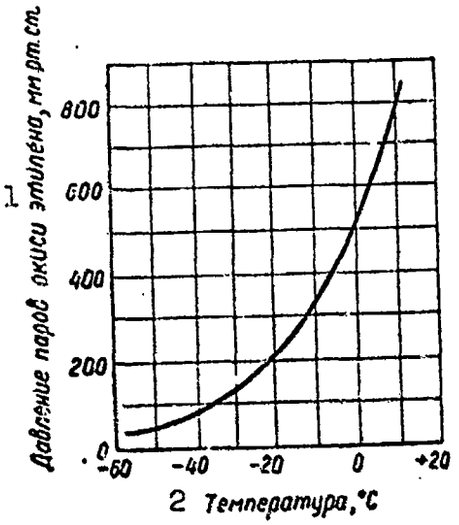


Fig. 291. Saturated ethylene-oxide vapor pressure as a function of temperature. 1) Vapor pressure of ethylene oxide, mm Hg; 2) temperature, °C.

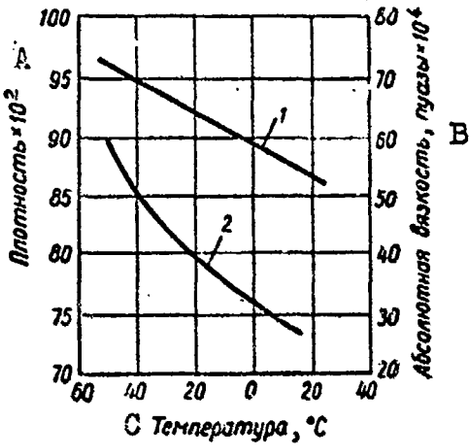


Fig. 292. Density and viscosity of ethylene oxide as functions of temperature. 1) Density; 2) viscosity; A) density x $10^2$; B) absolute viscosity, poises x $10^4$; C) temperature, °C.

TABLE 211

Pressure, Temperature of Decomposition, and Specific Thrust of Engine Operating on Ethylene Oxide

| 1 Давление в камере двигателя, ат | 2 Температура разложения, °С | 3 Удельная тяга, кг сек/кг |
|---|---|---|
| 20 | 1015 | 159,4 |
| 30 | 1027 | 168,0 |
| 40 | 1033 | 173,6 |
| 60 | 1039 | 180,7 |

1) Pressure in engine chamber, atm; 2) temperature of decomposition, °C; 3) specific thrust, kg·sec/kg.

The products of ethylene-oxide decomposition is a function of the

reaction conditions (the pressure in the combustion chamber, temperature, the catalyst, etc.).

Table 211 presents data on the temperature of decomposition and the specific thrust of an engine operating on ethylene oxide, at various temperatures [14, 15].

Ethylene oxide is stored in liquefied form in flasks or tanks, under excess pressure. Ethylene oxide is comparatively safe in use, but it exhibits a harmful effect on the human organism, as a result of which preventive measures must be taken and observed in handling this material.

In conclusion of this examination of propellants based on endothermic compounds we should point out that, generally speaking, the decomposition reactions as a source of energy are distinguished from oxidation reactions, for example, by a low thermal effect. The thermal effect is substantially increased when these compounds are used as oxidizers (hydrogen peroxide) or as combustibles (ethylene oxide, hydrazine), since in this case the heat of the decomposition reaction is added to the head of combustion.

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## Chapter 28

## FILTRATION OF FUELS

Aviation fuels are contaminated with mechanical impurities primarily during the transportation, pumping (through the fuel system), draining, and storage of the fuels. The mechanical impurities which enter the fuels consist primarily of ferric oxide (scale), sand, and carboniferous and fibrous substances.

Fuels are contaminated with mechanical impurities primarily as a result of inadequate hermetic sealing of tank cars and storage tanks, as a result of the improper cleaning of these tanks before filling them with fuel, and primarily as a result of the fact that in the majority of cases the tank cars, the storage tanks, and the manifolds (fuel systems) intended for aviation fuels have not been provided with protective anticorrosion coatings.

In view of the above-mentioned factors, as the fuel is moved from the petroleum refinery to the user, the quantity of mechanical impurities in the fuel increases. For example, in fuels arriving in railroad tank cars the content of mechanical impurities reaches 15-20 mg/l, whereas aircraft can be filled with a fuel containing no more than 1 mg/l of mechanical impurities. Therefore, before a fuel can be released for utilization in aircraft it must be subjected to special filtration and prolonged settling.

### FUELING OF AIRCRAFT

The volume of fuel tanks used in the latest types of gas-turbine engine aircraft employed in transport and military aviation abroad

ranges between 20,000 and 90,000 liters and is sometimes even higher (Table 212). Consequently, for the complete fueling of a single aircraft two railroad tank cars of fuel are required in certain cases.

At the present time aircraft fueling is carried out in two ways.

1. By means of high-capacity fuel trucks (up to 45,000 liters).

Powerful fuel pumps, supplying up to 4700 l/min of fuel are installed in large fuel trucks. In this case, no more than 15-20 minutes are required to fuel an aircraft.

TABLE 212

Volume of Fuel Tanks in Certain Types of Foreign Aircraft

| 1 Тип самолета | 2 Объем топливных баков самолета, л | 3 Скорость заправки топливом, л/мин | 4 Количество заправочных люков на самолете |
|---|---|---|---|
| 5 Вайкаунд | — | 1800 | 2 |
| 6 Каравелла-210 | 10400 | 1350 | 2 |
| 7 Бристоль-Британия-310 | 30000 | 1350 | 2 |
| 8 Хэвиланд-Комета-4 | 40800 | 2000 | 2 |
| 9 Боинг-707-120 | 65800 | 4700 | 4 |
| 10 Боинг-707 межконтинентальный | 89000 | 4700 | 4 |
| 11 Дуглас DC-8 межконтинентальный | 81700 | 3800 | 4 |

1) Type of aircraft; 2) volume of aircraft fuel tanks, liters; 3) fueling rate, l/min; 4) number of fuel inlets on aircraft; 5) Vaykaund [Viscount]; 6) Karavella [Caravelle]-210; 7) Bristol-Brittania-310; 8) Kheviland-Kometa [Havilland-Comet]; 9) Boing [Boeing]-707-120; 10) Boing [Boeing]-707 intercontinental; 11) Duglas [Douglas] DC-8 intercontinental.

2. Delivery of the fuel directly to the airfield through fuel pipelines. In recent years this system has gained widespread acceptance abroad. Underground fueling tanks have been installed at airfields at the aircraft-fueling stations. Each such underground tank is equipped with several flexible hoses by means of which an aircraft can be fueled through several fuel inlets simultaneously.

In the technical literature we find the opinion that this is the only method to resolve the problem of simultaneously fueling a large number of aircraft (particularly in-transit aircraft) at major airfields, because heavy fuel trucks take up so much space at an airfield that they occasionally disrupt the normal operation of the field.

DURATION OF AIRCRAFT FUELING

Regardless of the volume of fuel involved, no more than 30 minutes is permitted for the fueling of transport aircraft flying domestic and international routes in the majority of countries in Europe, Asia, and America. This time period includes 5 minutes for preparation and 2 minutes for the passage of the fuel through the aircraft tanks.

To reduce the fueling time, and this is particularly important for in-transit aircraft, a system of simultaneous aircraft fueling through several points (fuel inlets) (2-4) is employed as are high rates of fuel feed through each manifold (Table 213).

Depending on the quantity of fuel being delivered to the tanks of an aircraft, the minimum required fuel-feed speed to ensure an aircraft-fueling duration of no more than 30 minutes is selected. However,

TABLE 213

Rate and Duration of Aircraft Fueling

| 1 Скорость подачи топлива в баки самолета, л/мин | 2 Продолжительность заправки самолета | |
|---|---|---|
| | 3 емкость баков 27 000 л | 4 емкость баков 65 000 л |
| 2750 | 5 15 мин. 43 сек. | 30 мин. 43 сек. |
| 3550 | 13 » 30 » | 24 » 48 » |
| 4550 | 12 » 12 » | 21 » 12 » |
| 5450 | 11 » 20 » | 19 » 45 » |
| 6350 | 10 » 44 » | 17 » 6 » |

1) Rate of supplying fuel to aircraft tanks, l/min; 2) duration of aircraft fueling; 3) tank capacity; 4) tank capacity; 5) 15 min. 43 sec.

In view of certain difficulties in the removal of the static-electricity charge that arises at high pumping speeds and in the case of fuel filtration, it is desirable to maintain a fueling (supply) rate that, in actual practice, does not exceed 4700 l/min.

At a fuel-feed rate of 4700 l/min for the fueling of, for example, a Boeing-707 aircraft with a fuel-tank capacity of 89,000 liters no more than 27 minutes are required, and this satisfies completely the international norms for the duration of aircraft fueling.

METHODS OF EVALUATING FUEL PURITY

Fuel-system units for aircraft with gas-turbine engines are extremely sensitive to the presence of mechanical impurities, tars, and water in the fuel.

At the present time, both here and abroad, it is the practice to maintain that in order to provide for normal operation of the fuel- and automatic-system units of aircraft the fuel should contain no mechanical-impurity particles larger than 5 μ. The quantity of mechanical impurities should not exceed 1 mg/l of fuel.

Under operating conditions, prior to the release of a fuel for purposes of aircraft fueling, it is checked for the presence of water and mechanical impurities. The evaluation of fuel purity is carried out visually, and in the majority of cases without the use of any instruments or reagents.

The Method of Visual Fuel-Purity Evaluation Used in the Soviet Union

Before a fuel is released for purposes of aircraft fueling a 100-250 ml specimen is taken. The specifications state that this fuel specimen, poured into a glass cylinder 40-55 mm in diameter, should be transparent and should contain no water or extraneous impurities that are either in suspension or have settled to the bottom of the cylinder.

The cited method is far from perfect because a fuel that has been evaluated as pure may contain as much as 10 mg/l of mechanical impurities when analyzed gravimetrically. However, the method of visual fuel-purity evaluation is widely used in practice.

The Method of Visual Fuel-Purity Evaluation Used in Great Britain

In Great Britain the purity of an aviation fuel, released for aircraft fueling, is checked by a method of visual evaluation of the condition of the boundary of separation between the fuel and water. The essence of this method consists in the following.

A fuel specimen of about 100 ml is taken and poured into a glass cylinder into which an approximately equal quantity of pure distilled water is added. Then the fuel with the water is thoroughly agitated and left to settle for a period of 2-5 minutes.

After the fuel and water have completely separated, all of the mechanical impurities and undissolved tar and carbon substances (if such are contained in the fuel) are collected from the boundary of separation between the fuel and the water.

The condition of the fuel-water boundary of separation is evaluated in accordance with the following four-point system.

| Visual Evaluation of Fuel-Water Boundary of Separation | Points |
|---|---|
| Boundary of separation is transparent and pure | 1 |
| Several small bubbles around the periphery of the boundary of separation | 1b |
| Interlaced film with small quantity of mechanical-impurity particles at boundary of separation | 2 |
| Freely floating interlaced film and/or slight collection of scum at boundary of separation | 3 |
| Light interlaced film and/or heavy collection of scum at boundary of separation | 4 |

Fuels with a visual evaluation not lower than 1 or 1b are acceptable for aircraft fueling.

FUEL SETTLING

Settling as a method for removal of the basic mass of large mechanical-impurity particles and emulsified water from the fuel is sufficiently effective and is used on a widespread scale in engine operation in all countries.

In Great Britain, no fuel is released for aircraft fueling in transport aviation until it has been permitted to settle in a stationary tank. The following duration norms for fuel settling in airport tanks have been established.

1. For settling of aviation gasolines no less than 50 minutes per each meter of gasoline depth in the tank are required.

2. For the settling of jet fuels of the aviation-kerosene type no less than three hours and twenty minutes per each meter of fuel depth in the tank are required.

TABLE 214

Duration of Fuel Settling (According to Baldwin's Data)

| 1 Сорт топлива | 2 Продолжительность осаждения | |
|---|---|---|
| | 3 мелких капель воды | частиц механических примесей размером 4 5 мк |
| 5 Авиабензины | 8 59 мин. | 40 мин. |
| 6 Топливо JP-4 (типа Т-2) | 9 5 час. | 3 часа |
| 7 Топливо JP-1 (типа Т-1) | 10 " | 6 час. |

1) Type of fuel; 2) duration of settling; 3) small drops of water; 4) particles of mechanical impurities 5 μ in size; 5) aviation gasolines; 6) JP-4 fuel (type T-2); 7) JP-1 fuel (type T-1); 8) 59 minutes; 9) 5 hours.

It has been established experimentally that finely dispersed water and the tiniest particles of mechanical impurities (scale) settle

out very slowly and, consequently, it is difficult to remove these from the fuel even in the case of prolonged settling. At the same time, the higher the viscosity and density of the fuel (propellant), the slower the settling out of the mechanical-impurity particles and the drops of water and, consequently, the greater the time required for fuel settling (Table 214).

We can see from the cited table that small drops of water and mechanical impurities settle out from the T-1 type of jet fuel more slowly (by a factor of 9-10) than from aviation gasolines which are less dense and exhibit lower viscosity.

It is precisely for this reason that the removal of water and mechanical impurities from jet fuels by the settling method is substantially more difficult than in the case of aviation gasolines.

PARTICLE SIZE OF MECHANICAL FUEL IMPURITIES PRIOR TO FILTRATION

Even after prolonged settling an aviation fuel may contain substantial quantities of mechanical impurities. In individual cases the content of mechanical impurities in fuels, after settling, may attain 10 mg/l of the fuel.

In terms of size the mechanical impurities may vary greatly. Below we present a typical composition of mechanical impurities, extracted from aviation kerosene after settling.

| Content of Mechanical Impurities, % by Weight | Particle Size of Mechanical Impurities, μ |
|---|---|
| 12 | 1-5 |
| 12 | 5-10 |
| 14 | 10-20 |
| 23 | 20-40 |
| 30 | 40-80 |
| 9 | 80-200 |

FILTRATION OF FUELS

The basic source of contamination in aviation fuels is dust, sand, rust (scale) from tanks and fuel systems, etc.

To reduce contamination of fuels during storage and pumping at the airfields, in recent times it has become the widespread practice abroad to use tanks and fuel systems (manifolds) that have been covered with various anticorrosion coatings which, at the same time, provide for the hermetic sealing of the tanks.

These measures are particularly effective, since the basic source of fuel contamination with mechanical impurities (scale) is almost completely eliminated.

For the removal of mechanical impurities from a fuel which has been released for aircraft fueling, the fuels must be filtered and for this purpose special high-purity filters of various designs are employed. At the present time the following types of high-purity filters are being used: paper, metalloceramic, and screened filters, which remove all mechanical impurities greater in size than 5 μ from the fuel.

High-purity filters are installed not only on fuel trucks, but in the fuel system of an aircraft as well. This is done to prevent the entry of mechanical impurities into the fuel control unit, into the high-pressure pumps, and into the spray nozzles (injectors) of the gas-turbine engine.

In transport aviation in the USA it is generally held that a fuel must be purified of mechanical impurities before it enters the aircraft's tanks. Therefore, slightly coarser filters than those employed in the filtering process during aircraft fueling are always installed in aircraft fuel systems. For example, in fueling DC-8 aircraft the fuel is filtered through microfilters; this filter can remove all mechanical impurities that are larger than 5 μ in size, while high-purity filters designed to remove particles greater than 10 μ in size are installed in the fuel system of the DC-8 aircraft.

With this system of filtration all danger of clogging the aircraft's high-purity filters with mechanical impurities is removed.

To eliminate the danger of clogging the filters in a DC-8 aircraft with ice crystals provision has been made for the heating of the fuel, and as a result it is possible always to maintain a fuel temperature above $0^{\circ}$ in the vicinity of the filters.

Many factors affect the ability of the fuel to pass through the high-purity filters.

The small quantity of tars which can be found in standard jet fuels, and are generally identified as actual tars, virtually do not clog the filters.

However, it has been noted that if free water is present in a fuel, the tars associate with the drops of water and may settle out on the filter, thus causing the clogging of the filter pores. This comes about as a result of the fact that the products of fuel oxidation (tars), on associating with the drops of water, cause the latter to become sticky, and this explains their adhesion to one another, which results in the formation of a tar film on the filter. Therefore, in the filtration through high-purity filters of fuels that contain particularly large quantities of tars, we can sometimes observe the fouling of the filters with tars, and this serves to reduce the full-flow capacity of the filter. This phenomenon is particularly pronounced when filtration is carried out with paper microfilters.

Insoluble substances or contamination in a fuel impairs the full flow of fuel through the filter. However, the speed with which a filter is choked off and the reduction of fuel filterability are functions not only of the quantity, but of the nature of these impurities and insoluble substances. Sticky substances, capable of adhering to the surface of the filter or to clog its pores, have a particularly

pronounced effect in the reduction of fuel filterability.

Fuel filterability is impaired when the fuel is cooled below the cloud point, because of the crystallization of high-melting hydrocarbons.

We have by no means presented all of the factors which may have an effect on the ability of a fuel to pass through high-purity filters, since for a complete evaluation we would have to present a classification and all of the types of filtering elements in the filters.

If a fuel exhibits poor filterability as a result of the presence of insoluble substances in it, the addition of a small quantity of water to such a fuel would reduce the filterability even more.

The presence of dissolved (hygroscopic) water in a fuel at plus temperatures has no significant effect on the filterability of a fuel. The filterability of a "wet" fuel is sharply impaired by cooling as a result of the settling out of tiny drops of water and the formation of ice crystals which are held back by the filter.

Removal of Ice Crystals from a Fuel by Filtration

Ice crystals form in fuels as a result of the freezing of the water dissolved in the fuels when there is a sharp drop in fuel temperature during the winter. Sometimes these ice crystals come into the fuel from the outside in the form of rime, which has formed on the walls of the aircraft and storage tanks.

The shape and size of the ice crystals formed in the fuel are functions of the rate of cooling and the presence of extraneous mechanical impurities in the fuel.

Baldwin's projects [2] established that with rapid cooling of a fuel extremely small ice crystals (4-10 μ in size) are, as a rule, formed; with slow cooling of the fuel, the crystals will be larger in

size – of the order of 15-40 μ.

In the absence of mechanical impurities in the fuel, the ice crystals are basically small and slightly elongated. With the presence of mechanical impurities in the fuel, and particularly if these are of fibrous materials, the ice crystals are somewhat larger and they collect like small beads on the finest of the fibers.

Abroad it has become widespread practice to employ various designs of microfilters (paper, metalloceramic, and screened) for purposes of filtering aviation fuels, and these filters provide for the removal of impurities whose particle size is greater than 3-5 μ.

In the filtering of a fuel through such microfilters, the basic mass of the ice crystals can be removed from the fuel. In the filtering of a fuel through linen fi rs which provide for fuel filtration to 20 μ, only a portion of the ice crystals can be removed from the fuel.

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## Chapter 29

## FIRE CHARACTERISTICS OF FUELS

### GENERAL INFORMATION

The petroleum fuels used in aviation and automotive transport are easily ignitable combustible liquids whose vapors combine with air to form explosive mixtures.

Under operating conditions in automotive transport and in aircraft the fuel may serve as a source of fire in the following cases:

1) in the case of the flashing (ignition) of the fuel vapors by an open flame, a heated wire, or an electric spark;

2) in the case of autoignition of the fuel if it should happen to come into contact with a heated surface, given that the temperature of this surface will be higher than the autoignition temperature of the fuel;

3) in the case of the explosion of the fuel vapors in the gas space of the tanks or in some other closed space, or in the case of the appearance of a static-electricity discharge.

To evaluate the potential danger of fire from petroleum fuels, the following basic characteristics are employed:

1) the temperature limits for the formation of explosive fuel-vapor and air mixtures;

2) the concentration limits of explosive mixtures;

3) the autoignition temperature for a fuel in contact with a highly heated surface;

4) the flash point of the fuel.

## Combustion and Flame Propagation

One of the most important combustion characteristics of a fuel-air mixture is the rate of flame propagation. It is precisely this characteristic that to a significant extent determines the fire danger of a fuel.

At the temperature of the flash point and higher a combustible mixture forms over the open surface of a liquid fuel. If this mixture were to be ignited by an extraneous source, the flame would propagate over the surface of the liquid fuel at a rate of 1.2-1.4 m/sec.

In a fuel-air mixture held motionless in a closed tank or set in laminar motion the flame will be propagated at a rate of 0.3-0.6 m/sec. Under conditions of the turbulent motion of the mixture, depending on pressure, degree of turbulence, and composition of the mixture, the flame will propagate at a rate of 10-30 m/sec.

## Fuel Flash Point

The flash point of a fuel is the temperature at which the fuel vapors, heated in a special closed instrument, form a mixture with air

TABLE 215

Effect of Vapor Pressure of Jet Fuels on Flash Point

| 1 Топливо | 2 Давление паров при, 39° мм рт.ст. | 3 Вспышка (ГОСТ 1421-53), °С |
|---|---|---|
| 4 СССР | | |
| Т-1 | 25 | 30 |
| 5 ТС-1 | 35 | 28 |
| Т-2 | 75 | −4 |
| Т-2 | 100 | −14 |
| 6 Б-70 | 200 | −28 |
| Б-95/130 | 320 | −38 |
| 7 Англия | | |
| JP-5B | 10 | +60 |
| JP-1B | 15 | +38 |
| JP-4B | 100 | −14 |
| JP-4B | 160 | −23 |

1) Fuel; 2) vapor pressure at
[Key continued on following page]

[Key to Table 215 continued] 39° mm Hg; 3) flash (GOST 1421-53), °C; 4) USSR; 5) TS-1; 6) B-70; 7) Great Britain.

which flashes when a flame is brought close to it (GOST 6356-52). Research in recent times has established that given the fuel flash point established in a closed vessel, the vapor pressure of the fuel in question attains 7-10 mm Hg. Consequently, if the flash point of the T-1 fuel is equal to 30°, at 30° the pressure of its vapors would attain approximately 7-10 mm Hg. The flash point of the T-2 fuel is equal to −14°; this means that at −14° the vapor pressure of the T-2 fuel is equal to 7-10 mm Hg.

When the flash point is attained over the surface of the fuel an explosive concentration of fuel vapors in the air is formed. The flash point is a direct function of the fuel-vapor pressure: the higher the vapor pressure, the lower the flash point; this is clearly shown by the data presented in Table 215.

Classification of Fuel Fire Danger According to Flash Point

In the Soviet Union and abroad the fire danger of petroleum fuels is frequently classified in accordance with the flash point (Table 216),

TABLE 215

Classification of Fire Danger of Petroleum Fuels, Adopted by the Ministries of Sea and River Fleets of the Soviet Union

| 1Класс (разряд) огнеопасности топлив | 2Температура вспышки топлив, °С | |
|---|---|---|
| | руководство № 5-М, 1948 г. Министерства 3 морского флота | приказ № 108, 27/IV 1951 г. Министерства речного флота |
| I | 5 Ниже 28 | Ниже 28 |
| II | 28—65 | 28—45 |
| III | 6 65 и выше | 45—120 |

1) Class (category) of fuel fire danger; 2) fuel flash point, °C; 3) specification No. 5-M, 1948. Ministry of Sea Fleets; 4) order No. 108, 27 April 1951, Ministry of River Fleet; 5) below 28; 6) 65 and higher.

determined in a closed crucible. This classification is extremely imperfect and, at best, yields only an approximate idea as to the actual danger of fire represented by various grades of petroleum fuels. However, this method of fuel classification has been adopted in the USSR.

In accordance with this classification, a wide fractional-composition fuel of the T-2 type and aviation gasolines are graded as representing the I-class of fire danger. T-1 and TS-1 fuels, having a flash point of 28° and higher, are graded into the II-class of fire danger.

Temperature Limits for the Formation of Explosive Fuel-Vapor Mixtures

Explosive mixtures of fuel vapors with air are formed only within a definite temperature range.

TABLE 217

Temperature Limits for the Formation of Explosive Fuel Mixtures at Ground Level [1]

| 1 Топливо | 2 Температурные пределы образования взрывоопасных смесей, °С | |
|---|---|---|
| | 3 нижний | 4 верхний |
| А-66 | —39 | —8 |
| А-74 | —36 | —7 |
| Б-70 | —34 | —4 |
| 5 Б-91/115 | —38 | —5 |
| Б-95/130 | —37 | —5 |
| Б-100/130 | —34 | —4 |
| Т-2 | —18 | +14 |
| 6 ТС-1 | +28 | +57 |
| Т-1 | +27 | +59 |
| 7 Керосин осветительный (вспышка + 58°) | +57 | +87 |

1) Fuel; 2) temperature limits for the formation of explosive mixtures, °C; 3) lower; 4) upper; 5) B-91/115; 6) TS-1; 7) illuminating kerosene (flash) + 58°).

It is the practice to consider the upper and lower temperature limits. The lower temperature limit is the minimum temperature at which fuel vapors in a closed tank space will form an explosive mix

ture. With a further drop in fuel temperature the mixture is so leaned that it becomes difficult to ignite. The upper temperature limit is the maximum fuel temperature at which the mixture of the vapors with air still exhibits explosive characteristics. With a further increase in the temperature the mixture is markedly overenriched with fuel vapors and becomes incombustible.

At the lower temperature limit the vapor pressure of the fuel attains a certain magnitude at which, in the closed space of the tank, the formation of an explosive mixture is possible.

The temperature limits for the formation of explosive mixtures for various fuels are presented in Table 217.

FIRE CHARACTERISTICS OF DIESEL FUELS AND TRACTOR KEROSENES

Because of low vapor pressure and limited volatility, diesel fuels and tractor kerosenes are significantly less dangerous from the standpoint of fire than are gasolines. However, autoignition temperatures of these types of fuels are somewhat lower than the autoignition temperatures of ethylated gasolines. The temperature limits for the formation of explosive diesel-fuel mixtures lie substantially higher than the temperatures encountered during operation and, therefore, the formation of explosive concentrations of diesel-fuel vapors with air under normal conditions is difficult.

According to the data presented by M.G. Godzhello [sic], the minimum temperature for the formation of explosive mixtures of diesel-fuel vapors lies within a range of 57 to 76° (Table 218), and the upper boundary lies above 100°. Consequently, under normal conditions of operation the formation of explosive concentrations of diesel-fuel vapors is highly unlikely. However, we must take into consideration that in the case of the atomization or spraying of a diesel fuel explosive concentrations of its vapors may form at substantially lower tempera-

tures than are encountered in steady-state evaporation.

Tractor kerosenes are lighter in fractional composition and represent a greater fire danger.

In terms of fire danger they approach gasolines, and the illuminating kerosenes come close to diesel fuels (see Table 218).

TABLE 218

Fire Characteristics of Diesel Fuels and Kerosenes [1]

| 1 Топливо | Температура вспышки, °C | Температура самовоспламенения, °C | Температурные пределы образования взрывоопасных смесей, °C | |
|---|---|---|---|---|
| | | | 5 нижний | 6 верхний |
| 7 Дизельное | | | | |
| 8 ДЗ | 78 | 240 | 69 | 119 |
| 9 ДА | 64 | 330 | 57 | 105 |
| 10 ДС | 92 | 345 | 76 | 115 |
| 11 Л | 71 | 310 | 62 | 100 |
| 12 Керосин тракторный | 28 | 260 | 26 | 65 |
| | 30 | 240 | 30 | 54 |
| | 18 | 255 | 15 | 44 |
| | 4 | 290 | 5 | 35 |
| 13 Керосин осветительный | 48 | 265 | 45 | 86 |
| | 51 | 235 | 43 | 75 |
| | 58 | 250 | 57 | 87 |

1) Fuel; 2) flash point, °C; 3) autoignition temperature, °C; 4) temperature limits for the formation of explosive mixtures, °C; 5) lower; 6) upper; 7) diesel; 8) DZ; 9) DA; 10) DS; 11) L; 12) tractor kerosene; 13) illuminating kerosene.

## TEMPERATURE ZONES FOR THE FORMATION OF EXPLOSIVE MIXTURES AT VARIOUS ALTITUDES

For various grades of fuels exhibiting various saturated-vapor pressures and, consequently, exhibiting various degrees of volatility, sufficiently well-defined temperature ranges have been established and within these explosive mixtures may form at various altitudes.

With ascent as the external atmospheric pressure is reduced, fuel evaporation increases. As a result at some altitude an explosive mixture of fuel vapors and air is formed at substantially lower temperatures than would be the case on the ground, at normal atmospheric pre-

sure. Therefore, the temperature zone of explosive mixtures in terms of altitude shifts in the direction of lower temperatures.

TABLE 219

Beginning of Formation of Overenriched Mixtures

| 1 Топливо | 2 Давление паров топлива при 38°, мм рт. ст. | 3 Температурные пределы взрывоопасных смесей на высоте 15 000 м, °С | |
|---|---|---|---|
| | | 4 нижний | 5 верхний |
| Т-1 | 25 | 5 | 40 |
| ТС-1 | 35 | 0 | 20 |
| Т-2 | 100 | —22 | 5 |
| Б-70 | 200 | —30 | 15 |

1) Fuel; 2) fuel-vapor pressure at 38°, mm Hg; 3) temperature limits for explosive mixtures at an altitude of 15,000 m, °C; 4) lower; 5) upper.

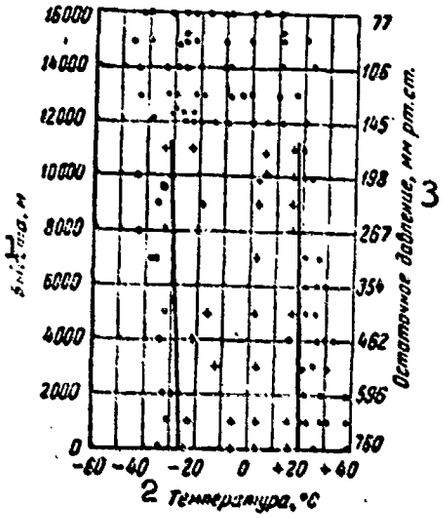


Fig. 293. Temperature limits for the formation of explosive mixtures of B-70 aviation gasoline vapor mixtures as a function of altitude (fuel-vapor pressure 200 mm Hg at 38°). 1) Altitude, m; 2) temperature, °C; 3) residual pressure, mm Hg.

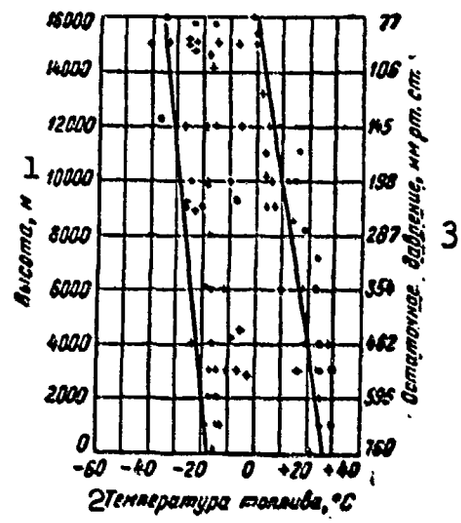


Fig. 294. Temperature limits for the formation of explosive T-1 fuel-vapor mixtures as a function of altitude (fuel-vapor pressure 45 mm Hg at 38°). 1) Altitude, m; 2) temperature of fuel, °C; 3) residual pressure, mm Hg.

There is a definite altitude for each type of fuel, depending on the pressure of its vapors and its volatility, i.e., a definite degree of rarefaction above which highly overenriched mixtures with unstable explosive characteristics begin to form (Table 219).

The temperature zones for the formation of explosive mixtures of various types of fuels are presented in the form of four graphs (Figs. 293-296). The two lines on each graph denote the zone of explosive mixtures. The right-hand line denotes the region of overenriched mixtures, while the left-hand line denotes the region of lean mixtures.

We can see from the cited graphs that the zone of explosion dangers for mixtures of T-1 fuel on the ground lies in a range between 25-65°; for TS-1 fuel, in a range between 15-60°; for T-2 fuel, between -10 and +40°; and for B-70 aviation gasoline, between -25 and +20°. With increasing altitude, the zone of explosion danger converges slightly and shifts in the direction of lower temperatures.

At an altitude of 11,000 m for B-70 aviation gasoline (Fig. 293), at an altitude above 15,000 m for T-1 (Fig. 294) and TS-1 (Fig. 295) fuels, and at an altitude in excess of 14,000 m for T-2 fuel (Fig. 296) the explosive danger of the mixtures becomes unstable as a result of the overenriching of the mixtures because of pronounced fuel evaporation.

However, all of these considerations pertain to the formation of explosive mixtures in aircraft fuel tanks in which there is a certain quantity of liquid fuel. A somewhat different picture is observed in evacuated fuel tanks in which a certain quantity of fuel always remains. The volume of these tanks may also be filled with an explosive mixture. Here we find a certain analogy with the situation observed in gasoline storage tanks: an empty gasoline barrel is always regarded as representing a danger of explosion and it is recommended that such a barrel be handled with extreme care.

The question arises, to what altitude is the danger of explosion in mixtures in evacuated aircraft fuel tanks still present? It is not possible to give a precise answer to this question, since this will

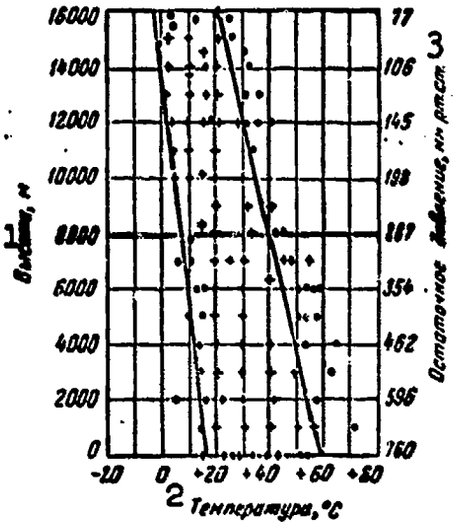


Fig. 295. Temperature limits for the formation of explosive mixtures of TS-1 fuel-vapor mixtures as a function of altitude (pressure of fuel vapors 50 mm Hg at 38°). 1) Altitude, m; 2) temperature, °C; 3) residual pressure, mm Hg.

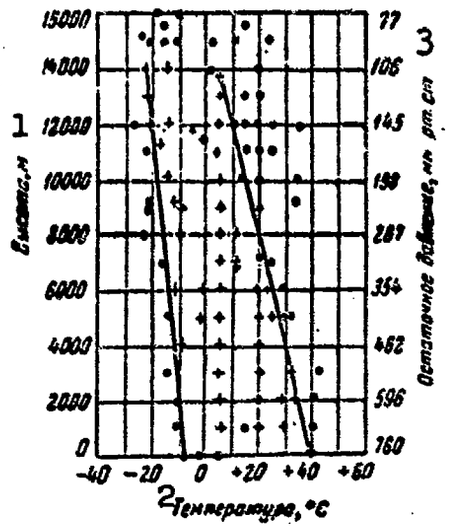


Fig. 296. Temperature limits for the formation of explosive mixtures of T-2 fuel vapors as a function of altitude (pressure of fuel vapors 100 mm Hg at 38°). 1) Altitude, m; 2) temperature, °C; 3) residual pressure, mm Hg.

pend not only on the physicochemical characteristics of the fuel, but on the quantity of fuel remaining in the tanks as well. Since the residue of fuel in evacuated aircraft tanks cannot always be determined exactly, it is, in fact, impossible to determine to which altitude the danger of explosion for the fuel-vapor mixture in these tanks is preserved.

To ensure against accidents, we can assume that explosive mixtures may be present in evacuated aircraft tanks at virtually all operational altitudes during flight.

Therefore, preventive measures must be taken.

Foam Formation in Tanks and the Danger of Explosion that These Foams Represent

A fuel poured into an aircraft tank is always saturated with dissolved air. It has been established that the lower the surface tension

TABLE 220

Solubility of Air in Fuels

| 1 Топливо | 2 Удельный вес при 21° | 3 Поверхностное натяжение при 21°, дн/см | 4 Растворимость воздуха в топливе при 21°, % объемн. |
|---|---|---|---|
| 5 Газойль | 0,870 | 26,8 | 9,7 |
| 6 Авиакеросин | 0,780 | 23,4 | 17,2 |
| 7 Авиабензин | 0,723 | 18,4 | 22,8 |

1) Type fuel; 2) specific weight, at 21°; 3) surface tension, at 21°, dynes/cm; 4) solubility of air in fuel at 21°, % by volume; 5) gas oil; 6) aviation kerosene; 7) aviation gasoline.

of the fuel, the more air can be dissolved in the fuel. This situation is clearly illustrated by the research data of L.D. Derri [sic] (Table 220).

As the aircraft climbs and the outside atmospheric pressure diminishes, the air dissolved in the fuel gradually begins to separate out. It has been established that the separation of the air from the fuel is substantially speeded up through mechanical agitation of the fuel.

When booster pumps are turned on during flights at great altitudes, the separation of the dissolved air from the fuel sometimes takes place so violently that a large layer of foam is formed at the surface of the fuel in the aircraft tanks.

B.V. Poul'ston [sic] established experimentally that the foam formed in the manner described above represents a great danger of explosion and combustion even at comparatively low temperatures. A flame is propagated very rapidly through this foam and the pronounced danger of explosion that this foam represents can be explained by the fact that there is always an increased concentration of oxygen in the air which is separated from the fuel (the solubility of oxygen at 20° is greater by a factor of approximately 1.6 than the solubility of nitrogen, and therefore the air separated from the fuel is always overe...

riched with oxygen).

CONCENTRATION LIMITS OF EXPLOSIVE FUEL-VAPOR MIXTURES

The limit concentrations of fuel vapors in air, at which ignition of the mixture and flame propagation are possible, are referred to as the concentration ignition limits.

Table 221 shows the experimental data for the concentration limits of explosive mixtures of various types of aviation gasolines and jet fuels.

TABLE 221

Concentration Limits of Explosive Mixtures of Vapor Fuels in Air [1]

| 1 Топливо | 2 Плотность, г/см³ | 3 Концентрационные пределы взрывоопасных смесей, % объемн. | |
|---|---|---|---|
| | | 4 нижний | 5 верхний |
| А-66 | 0,728 | 0,76 | 5,03 |
| А-74 | 0,730 | 0,79 | 5,16 |
| Б-70 | 0,745 | 0,79 | 5,16 |
| Б-91/115 | 0,729 | 0,89 | 5,46 |
| Б-95/130 | 0,736 | 0,95 | 5,48 |
| Б-100/130 | 0,728 | 0,96 | 5,48 |
| Т-2 | 0,765 | 1,1 | 6,8 |
| ТС-1 | 0,779 | 1,2 | 7,1 |
| Т-1 | 0,813 | 1,4 | 7,5 |
| 6 Керосин осветительный (вспышка +58°) | 0,834 | 1,4 | 7,5 |

1) Fuel; 2) density, g/cm$^3$; 3) concentration limits of explosive mixtures, % by volume; 4) lower; 5) upper; 6) illuminating gasoline (flare + 58°).

Flash Point as Function of Fuel-Vapor Pressure

The flash point of a fuel actually indicates the lowest temperature at which the formation of explosive mixtures is possible, and the lower limit for the formation of explosive mixtures indicates the minimum concentration of fuel vapors in the air, at which the combustion of the mixture is possible.

Using the above-indicated relationship we can find the lower limit of explosive mixtures according to the flash point of the fuel or we

can calculate the flash point on the basis of the explosive-mixture limit.

Knowing the lower concentration limit for the formation of explosive mixtures we can calculate the fuel-vapor pressure at which flashing may take place:

$$P_{t.v.} = \frac{vP}{100},$$

where $P_{t.v}$ is the fuel-vapor pressure at the flash point, in mm Hg; v is the lower concentration limit for the formation of explosive mixtures, in % by volume; P is the pressure of the fuel-vapor mixture with air, in mm Hg.

Example. Find the gasoline vapor pressure at which flashing takes place, if the lower concentration limit for the formation of explosive mixtures is known to be 0.98% by volume:

$$P_{t.v.} = \frac{vP}{100} = \frac{0.98 \cdot 760}{100} = 7.45 \text{ mm Hg.}$$

Consequently, gasoline flashing will take place when a vapor pressure of 7.45 mm Hg is attained.

Determination of Fuel-Vapor Content in Air

If we know the temperature of the fuel and the pressure of its saturated vapors at a given temperature, the concentration of fuel vapors in the air can be calculated in accordance with the following formula:

$$v = \frac{P_t \cdot 100}{P_{at}},$$

where v is the concentration of fuel vapors in the air, in % by volume; $P_t$ is the saturated vapor pressure, in mm Hg; $P_{at}$ is the pressure of the fuel-vapor mixture with air (in the majority of cases, it is equal to atmospheric pressure), in mm Hg.

Example. Determine the volumetric concentration of T-2 fuel va-

pors in an aircraft tank at a temperature of 20°. The pressure of saturated fuel vapors at 20° is equal to 40 mm Hg:

$$v = \frac{40 \cdot 100}{760} = \frac{4000}{760} = 5{,}26\% \text{ by volume.}$$

The volumetric concentration of fuel vapors in the air can be recalculated into mass concentration by the following formula:

$$g = \frac{vm}{2{,}24}.$$

Example. The volumetric concentration of T-2 fuel vapors in air at 20° is equal to 5.26%. Calculate the mass concentration, if the mean molecular weight of the fuel is 150.

$$g = \frac{vm}{2{,}24} = \frac{5{,}26 \cdot 150}{2{,}24} = 352 \text{ mg/l} = 0{,}352 \text{ g/l}.$$

AUTOIGNITION TEMPERATURE OF FUELS

Autoignition is an important characteristic in determining the danger of fire from fuels. Under operational conditions, autoignition is possible if a liquid fuel or its vapors come into contact with a highly heated surface. We know from practical experience that such cases are possible when the hermetic sealing of the fuel manifolds in an engine frame is broken. From the standpoint of fire safety it is extremely important to know the temperature to which a metallic surface must be heated before it can cause the ignition of any fuel coming into contact with this surface.

The autoignition temperature of a fuel is not constant; it is a function of the evaluation method employed.

The chemical composition of the fuel has a significant effect on the autoignition temperature. In the majority of cases, the higher the molecular weight of the fuel and the heavier its fractional composition, the lower the autoignition temperature. Ethylated gasolines, as a rule, exhibit a higher autoignition temperature than those that are

TABLE 222

Autoignition Temperature of Aviation Fuels

| 1 Топливо | 2 Температура вспышки, °С | 3 Температура воспламенения топлива, °С | 4 Температура нагретой плиты, вызывающая воспламенение топлива, °С |
|---|---|---|---|
| Т-1 | +30 | 220 | 325 |
| ТС-1 | +28 | 218 | 325 |
| Т-2 | —12 | 233 | 330 |
| Б-70 | —30 | 331 | 430 |

1) Fuel; 2) flash point, °C; 3) fuel ignition temperature, °C; 4) temperature of heated plate causing fuel ignition, °C.

not ethylated, because of the presence of TES [TEL – tetraethyl lead].

We can see from Table 222 that the autoignition temperature of B-70 aviation gasoline is 111° higher than the autoignition temperature of the T-1 fuel. This can be explained by the fact that the fractional composition of the T-1 fuel is heavier than the fractional composition of the B-70 gasoline.

It was brought out during these experiments that for the TS-1 fuel the temperature of the heated metal plate must be 325° in order for the fuel to experience autoignition in coming into contact with the plate; for the B-70 aviation gasoline this temperature would be approximately 430°C. Thus it was established experimentally that if a fuel comes into contact with a heated surface whose temperature ranges between 325 and 425°, ignition may take place and result in a fire.

The autoignition temperatures of various types of domestically produced fuels are actually quite close to those that were derived in the USA in accordance with the drop method. This can be seen from the following example.

JP-1 . . . . . 228
JP-3 . . . . . 228
JP-4 . . . . . 242
B-73 . . . . . 258
B-100/130 + TEL . . . . . 440

## Effect of Altitude on Autoignition Temperature of Aviation Fuels

With an increase in pressure, the autoignition temperature of fuels diminishes, and vice versa. Table 223 shows data derived by

TABLE 223

Effect of Altitude on Ignition Temperature of Fuels

| 1 Топливо | 2 Задержка воспламенения при 742 мм рт. ст., сек. | 3 Температуры самовоспламенения, °C | |
|---|---|---|---|
| | | 4 давление 742 мм рт. ст. (на земле) | 5 давление 370 мм рт. ст. (высота 5700 м) |
| 6 Авиабензин 100/130 | 3 | 440 | 553 |
| JP-1 | 120 | 228 | 462 |
| JP-3 | 187 | 238 | 449 |
| JP-4 | 185 | 242 | 444 |

1) Fuel; 2) ignition lag at 742 mm Hg, sec; 3) autoignition temperature, °C; 4) pressure 742 mm Hg (on the ground); 5) pressure 370 mm Hg (altitude 5700 m); 6) aviation gasoline 100/130.

M. Zabetakis [sic]* on the effect that altitude (reduction in pressure) exerts on the autoignition temperature of aviation fuels.

## AUTOIGNITION OF COMBUSTIBLE LIQUIDS

There are a number of combustible liquids which are capable of intense oxidation in air at normal temperatures (16-20°). Under certain conditions, when the quantity of heat liberated during the oxidation process exceeds the heat transfer to the external medium, autoignition of the oxidizing liquid may take place. Such liquids are referred to as hypergolic and they are conventionally divided into two groups.

The first group consists of liquids that tend to autoignition when in contact with air: vegetable oils, turpentine, and certain animal fats in films on developed surfaces of fibrous materials (cotton and cotton waste, etc.).

The second group consists of liquids that tend to autoignition

only in contact with or in chemical interaction with other substances; for example, ethylene glycol and glycerine in contact with potassium permanganate, as well as alcohols in contact with peroxides, etc.

In practice the autoignition capacity of vegetable oils is determined according to the iodine number. It is generally maintained that a liquid with an autoignition tendency represented by an iodine number above 100 is dangerous from the standpoint of fire.

The Rate at Which a Fuel Burns off from a Surface

The rate at which fuels burn off a surface is determined by the mass of fuel consumed per unit surface per unit time, e.g., $kg/m^2 \cdot hr$.

TABLE 224

The Rate at Which a Fuel Burns off a Surface in Tanks [2]

| 1 Топлива | 2 Плотность топлива, г/см³ | 3 Скорость выгорания топлива с поверхности в резервуарах малого диаметра | | 4 Теплонапряжение зеркала испарения топлива, ккал/м² час |
|---|---|---|---|---|
| | | 5 мм/мин | 6 кг/м² час | |
| 7 Авиационный бензин | 0,730 | 2,10 | 91,98 | 12 390 |
| 8 Автомобильный бензин | 0,770 | 1,75 | 80,85 | 12 300 |
| 9 Керосин . . . . . | 0,835 | 1,10 | 55,11 | 10 710 |

1) Fuel; 2) density of fuel, $g/cm^3$; 3) rate at which a fuel burns off from a surface in small-diameter tanks; 4) heat liberation from evaporation surface of fuel, $kcal/m^2 \cdot hr$; 5) mm/min; 6) $kg/m^2 \cdot hr$; 7) aviation gasoline; 8) automotive gasoline; 9) kerosene.

In certain cases the rate of burning is expressed by the so-called linear burning rate which represents the height of the fuel layer (mm) burned per unit time (min).

Depending on density and fractional composition, the rate at which a fuel burns off from a surface will vary: the lower the density of the fuel, the faster the burning rate (Table 224).

Prevention of Fuel-Vapor Explosions in Aircraft Tanks

On certain types of foreign military jet aircraft, an inert ga

is introduced into the ullage of fuel tanks in order to prevent the explosion of fuel vapors.

The quantity of gas which must be introduced into the fuel-vapor mixture in order to render it safe from explosion was the subject of numerous investigations. Table 225 presents some data.

TABLE 225

Fire-Extinguishing Concentrations of Gases to Prevent Explosions of Gasoline and Kerosene Vapors (Concentration, in % of Air)

| 1 Газ | 2 Необходимое количество газа, % объемн. | |
|---|---|---|
| | 3 по данным П. Г. Демидова | 4 по данным Юрсенева |
| 5 Углекислый газ . . . . . | 23,0 | 21,2 |
| 6 Азот . . . . . | 31,0 | 30,8 |
| 7 Бромистый метил . . . . | 4,0 | — |
| 8 Четыреххлористый углерод | 7,5 | 8,0 |

1) Gas; 2) required quantity of gas, % by volume; 3) after P.G. Demidov; 4) after Yursenev; 5) carbon dioxide; 6) nitrogen; 7) methyl bromide; 8) carbon tetrachloride.

We can see from these data that the fire-extinguishing effect of halogen derivatives is several times greater than that of carbon dioxide or nitrogen. The varying fire-extinguishing efficiency of the gases is explained by P.G. Demidov by the various mechanisms with which they affect burning. In the opinion of P.G. Demidov, the introduction of methyl bromide or carbon tetrachloride into the burning zone of fuel-air mixtures disrupts the combustion (an exothermic reaction) and the liberation of heat in the reactions taking place is sharply reduced; as a result burning ceases.

The fire-extinguishing effect of carbon dioxide and nitrogen consists in the reduction of the oxygen concentration in a mixture to a point at which continued burning is impossible. According to the data of this author, with the introduction of carbon dioxide into the burn-

ing mixture, combustion is brought to a stop when the oxygen content falls below 14-18%, and with the introduction of methyl bromide the burning ceases as soon as the oxygen content is reduced to 20.6% [3].

The utilization of an inert gas to fill the free space in fuel tanks is, naturally, associated with the auxiliary equipment that must be installed aboard an aircraft. The over-all weight of the gas and the equipment, on the average, amounts to 1 kg for each 100 liters of fuel-tank capacity. This means that for an aircraft with a fuel-tank capacity of 30,000 liters, the weight of the gas and equipment amounts to about 300 kg.

"ELECTRIFICATION" OF FUELS

During the transportation of jet and diesel fuels over water or by railroad, during the pumping of these fuels, when these fuels are poured in and out of a container, as well as during the fueling of aircraft and cars, "mysterious" cases of explosions and fires occur rather frequently. Investigations conducted by the American Petroleum Institute have shown that a significant part of these "mysterious" or difficult-to-explain explosions and fires during operations with petroleum products can be attributed to static electricity.

The control of static electricity and the development of preventive measures is, in many cases, made difficult by the absence of a clear understanding regarding the mechanism by which static-electricity charges are formed in petroleum products.

At the present time the mechanism by which a charge of static electricity is formed during the handling of petroleum products has been thoroughly studied. It has been established that under certain conditions, even in a fuel that is kept in a fixed state, the formation of static electricity is possible and the discharge of this static electricity is capable of producing an explosion and fire at

the petroleum refinery and petroleum storage area, if the required preventive measures are not implemented.

The investigations that were carried out and a detailed study of the facts relating to the occurrence of explosions and fires as a result of static electricity made it possible to establish the following six factors responsible for the formation of a static-electricity charge in fuels.

I. WITH FUEL IN MOTION

1. In the case of friction between a liquid fuel and the solid surface of the manifold, the walls of the tank, and the filter.

2. In the case of friction between fuel particles, during the passage of the fuel through a medium of other liquids such as, for example, water, etc.

3. In the case of the passage of drops of finely atomized fuel through air or a vapor-air mixture.

II. WITH FUEL NOT IN MOTION

4. In the case of solid suspended particles settling out of the fuel.

TABLE 226

Factors Responsible for the Formation of Static Electricity and the Occurrence of Fire

| 1 Причины образования заряда статического электричества | 2 Пожары | |
|---|---|---|
| | 3 количество | % |
| 4 Перекачка и перемешивание топлива | 37 | 58 |
| 5 Неправильный слив и заполнение резервуаров топливом | 10 | 16 |
| 6 Выпуск сырого водяного пара в топливо | 6 | 10 |
| 7 Большая скорость слива и перекачки топлива | 4 | 6 |
| 8 Замыкание электричества на корпус резервуара | 4 | 6 |
| 9 Распыление струи топлива в воздух над поверхностью топлива | 1 | 2 |

TABLE 226 (Continued)

| | | | |
|---|---|---|---|
| 10 | Удар молнии (работа во время грозы) . . . . . | 1 | 2 |
| 11 | Всего . . . . . | 63 | 100 |

1) Factors responsible for the formation of a static-electricity charge; 2) fires; 3) quantity; 4) pumping and agitation of fuels; 5) improper drainage and filling of fuel tanks; 6) injection of raw steam into the fuel; 7) fast drainage and fuel pumping; 8) completing an electric circuit on the fuel tank; 9) atomization of a stream of fuel into the air above the surface of the fuel; 10) the striking of a lightning bolt (work during a storm); 11) total.

5. In the case of liquid suspended particles such as, for example, drops of water or other chemical substances settling out of the fuel, as well as in the case of the passage of bubbles of air, vapors of light hydrocarbons, etc., passing through a layer of liquid fuel.

6. In the case of the passage of drops of water (rain), snow flakes, etc., through the vapor-air space.

The American Petroleum Institute studied in detail 63 cases in which fuel tank cars exploded, resulting in fires, and the factors responsible for the formation of the static-electricity charge were determined (Table 226).

Specific Electrical Conductivity of Fuels

The quantity of electricity which passes through 1 $cm^2$ of a cross section of fuel in 1 sec with an electric-field voltage of 1 v per 1 cm is referred to as the specific electrical conductivity of fuel; it is expressed in the following units: $ohm^{-1}$ $cm^{-1}$.

It has been established experimentally that the capacity of a fuel to form static electricity during pumping is a function of the fuel's specific electrical conductivity (Table 227).

The rate at which the static-electricity charge is dissipated

TABLE 227

Rate of Static-Electricity Formation During Fuel Pumping as a Function of Specific Electrical Conductivity

| 1 Удельная электропроводность топлива, $ом^{-1}\ см^{-1}$ | 2 Количество разрядов статического электричества в течение 10-минутной перекачки (7 кв) |
|---|---|
| $1\times10^{-15}$ | 1 |
| $5\times10^{-15}$ | 35 |
| $1\times10^{-14}$ | 110 |
| $5\times10^{-14}$ | 500 |
| $1\times10^{-13}$ | 600 |
| $5\times10^{-13}$ | 550 |
| $1\times10^{-12}$ | 250 |
| $5\times10^{-12}$ | 2 |
| $1\times10^{-11}$ | 0 |

1) Specific electrical fuel conductivity, $ohm^{-1}\ cm^{-1}$; 2) number of static-electricity discharges during a 10-minute pumping (7 kv).

(drops) is directly proportional to the specific electrical conductivity of the fuel: the lower the electrical conductivity, the slower the dissipation of the static-electricity charge that has formed (Table 228).

Various types of jet, aviation, and motor fuels exhibit various capacities to form static electricity. This phenomenon is illustrated rather clearly by the data cited below, where we can see the time required for the formation of a static-electricity charge during a 10-minute period of pumping (voltage, 7 kv):

| | |
|---|---|
| Isooctane, n-heptane, cetane | 0-12 |
| Toluene and xylene | 14-50 |
| Aviation gasolines and automotive gasolines | 41-59 |
| JP-4 jet fuel | 1-71 |
| Unpurified kerosene | 7-82 |
| JP-5 jet fuel | 10-140 |
| Diesel fuel | 5-420 |

TABLE 228

Rate of Static-Electricity Charge Dissipation as Function of Specific Electrical Conductivity of Fuel

| 1 Удельная электропроводность топлива, $ом^{-1}$ $см^{-1}$ | 2 Время снижения заряда статического электричества на 50%, сек. |
|---|---|
| $10^{-15}$ | 130 |
| $10^{-14}$ | 13,0 |
| $10^{-13}$ | 1,30 |
| $10^{-12}$ | 0,13 |
| $10^{-11}$ | 0,013 |

1) Specific electrical conductivity of fuel, $ohm^{-1}$ $cm^{-1}$; 2) time required to reduce static-electricity charge by 50%, sec.

It has been established by investigation that the time required for the formation of static electricity is significantly affected by many operational factors such as, for example, the pumping rate, the presence of mechanical impurities in the fuel, the presence of water and air, as well as the conditions of storage and temperature.

Influence of Fuel Pumping Rate

All other conditions being equal, the the higher the pumping or fuel-drainage rate, the greater the quantity of static electricity

TABLE 229

Influence of Fuel Pumping Rate on Formation of Static Electricity

| 1 Реактивное топливо | 2 Количество разрядов статического электричества (7кв) за 10-минутную перекачку | |
|---|---|---|
| | 3 скорость перекачки 500 мл/мин | скорость перекачки 1500 мл/мин |
| JP-4 (A) | 24 | 138 |
| JP-5 (B) | 16 | 84 |
| JP-5 (C) | 8 | 28 |
| JP-4 (D) | 3 | 14 |

1) Jet fuel; 2) number of static-electricity discharges (7 kv) during a 10-minute pumping period; 3) pumping rate, 500 ml/min.

formed. This quantitative relationship is clearly illustrated by the laboratory-investigation data presented in Table 229.

Influence of Jet Fuel Purity

Mechanical impurities in a fuel have a significant effect on the speed with which static electricity is formed: the purer the fuel, the

TABLE 230

Influence of Jet-Fuel Purification on Formation of Static Electricity During Pumping

| 1 Способы очистки топлив | 2 Удельная электропроводность, $ом^{-1}$ $см^{-1}$ | 3 Количество разрядов статического электричества во время 10-минутной перекачки (7 кв) |
|---|---|---|
| 4 Топливо JP-5 без очистки | $1.8\times10^{-12}$ | 40 |
| 5 Перколяционная очистка силикагелем | $0.005\times10^{-12}$ | 0 |
| 6 Контактная очистка глиной | $0.009\times10^{-12}$ | 0 |
| 7 Гидроформинг | $0.005\times10^{-12}$ | 5 |
| 8 Микрофильтрация | $0.013\times10^{-12}$ | 19 |

1) Methods of fuel purification; 2) specific electrical conductivity, $ohm^{-1}$ $cm^{-1}$; 3) number of static-electricity discharges during 10-minute pumping period (7 kv); 4) JP-5 fuel without purification; 5) percolation purification with silica gel; 6) contact purification with clay; 7) hydraulic forming; 8) microfiltration.

slower the formation of static electricity.

Below we present data on the effect exerted by the presence of mechanical impurities in a jet fuel on the formation of static-electricity discharges (7 kv):

JP-5 fuel without mechanical impurities . . . . . 15

JP-5 fuel with finely fragmented tank-car deposits . . . . . 27

Mechanical impurities can be removed from a fuel by filtration, at the same time reducing the tendency of the fuel to form static

electricity during pumping or aircraft fueling (Table 230).

Influence of Water and Air Bubbles

It has been established that in the presence of dissolved and dispersed water in a fuel there is a substantial increase in the formation of static electricity. However, the presence of an individual layer of water at the bottom of the tank sometimes exerts no effect whatsoever or reduces the formation of static electricity. Under the influence of water in a jet fuel the following quantities of static electricity (7 kv) are formed:

| | |
|---|---|
| Dried aviation kerosene | 60 |
| Aviation kerosene with dissolved water | 120 |
| Aviation kerosene + 0.5% finely dispersed water | 150 |
| Aviation kerosene + 0.5% of water at the bottom of the tank car | 0 |

Given the presence of air bubbles in the fuel, as a rule, there is an increase in the tendency of the fuel to form static electricity during pumping, and this can be seen from the cited data (the air-feed rate into the fuel is 500 ml/min).

| | |
|---|---|
| JP-5 fuel without air | 7 |
| JP-5 fuel with large air bubbles | 12 |
| JP-5 fuel with small air bubbles | 22 |

Effect of Temperature

It has been established experimentally that in the majority of cases in which a fuel is heated from $10^{\circ}$ to $40^{\circ}$ the tendency of the fuel to form static electricity weakens (Table 231). But individual cases were noted in which the same heating resulted in more pronounced formation of static electricity [JP-4 (D)].

Significant chemical changes occur in the fuel under the action of high temperature; in certain cases insoluble sedimentation forms

TABLE 231

Effect of Fuel Heating on the Formation of Static Electricity

| 1 Реактивное топливо | 2 Количество разрядов статического электричества при температуре перекачки (10 мин.), °С | | |
|---|---|---|---|
| | 10 | 27 | 40 |
| JP-4 (A) . . . . . | 3 | 2 | 0 |
| JP-4 (B) . . . . . | 176 | 135 | 10 |
| JP-4 (C) . . . . . | 125 | 118 | 23 |
| JP-4 (D) . . . . . | 153 | 230 | 553 |

1) Jet fuel; 2) number of static-electricity discharges at the pumping temperature (10 min.), °C.

the fuel. At the present time, in the USA, the thermal stability of jet fuels is generally determined by means of a "Koker" instrument which determines the quantity of sedimentation formed in the fuel.

Investigations have shown that a jet fuel that has passed the thermal-stability test on the "Koker" device, in which it was heated to 150°, substantially increased its capacity to form static electricity, and this can, apparently, be explained by the formation of the tiniest of solid carbon particles in the fuel (Table 232).

An analogous situation is observed in the case of the synthetic addition of carbon substances to the jet fuel. Even the slightest addition of petroleum asphalt (0.005-0.0005%) results in a pronounced increase in the ability of the fuel to form static electricity during pumping (Table 233).

As we can see from Table 233, the sediment that does not dissolve in ligroin brings about the more pronounced tendency of the fuel to the formation of static electricity.

TABLE 232

Effect of High-Temperature Treatment of Fuel on the Formation of Static Electricity

| 1 Реактивное топливо | 2 Количество разрядов статического электричества (7 кв) при 10-минутной перекачке | |
|---|---|---|
| | 3 до определения термической стабильности | 4 после определения термической стабильности (нагрев топлива до 150°) |
| JP-4 (A) | 5 | 13 |
| JP-4 (B) | 13 | 30 |
| JP-4 (C) | 81 | 190 |

1) Jet fuel; 2) number of static-electricity discharges (7 kv) during 10-minute pumping; 3) prior to determination of thermal stability; 4) after determination of thermal stability (fuel heated to 150°).

TABLE 233

Effect of the Addition of Carbon Matter (Petroleum Asphalt) to a Fuel on the Formation of Static Electricity

| 1 Топливо | 2 Удельная электропроводность, $ом^{-1}\ см^{-1}$ | 3 Количество разрядов статического электричества |
|---|---|---|
| 4 Топливо JP-5 без добавок | $0{,}011\times10^{-12}$ | 4 |
| 5 Топливо JP-5 + 0,005% нефтяного битума . . . . . | $0{,}5\times10^{-12}$ | 130 |
| 6 Топливо JP-5 + 0,005% нефтяного битума, растворимого в лигроине . . . . | $1{,}9\times10^{-12}$ | 131 |
| 7 Топливо JP-5 + 0,0005% нефтяного битума, не растворенного в лигроине | $1{,}20\times10^{-12}$ | 112 |
| 8 Изооктан без добавок . . | $0{,}0008\times10^{-12}$ | 1 |
| 9 Изооктан + 0,0005% нефтяного битума . . . . | $0{,}0084\times10^{-12}$ | 2 |

1) Fuel; 2) specific electrical conductivity, $ohm^{-1}cm^{-1}$; 3) number of static-electricity discharges; 4) JP-5 fuel without additives; 5) JP-5 fuel + 0.005% petroleum asphalt; 6) JP-5 fuel + + 0.005% petroleum asphalt, dissolved in ligroin; 7) JP-5 fuel + 0.0005% petroleum asphalt, not dissolved in ligroin; 8) isooctane without additive; 9) isooctane + 0.0005% petroleum asphalt.

Effect of Fuel Oxidation During Storage

There is a pronounced increase in the capacity to form static electricity during pumping of a fuel which oxidized during storage and in which the content of potential tars increased (Table 234).

TABLE 234

Effect of Fuel Oxidation on the Formation of Static Electricity During Pumping (Fuel Stored in a 200-Liter Barrel at 77°)

| 1 Продолжительность хранения, (дни) | Содержание потенциальных смол в топливе, 2 мг/100 мк | 3 Количество разрядов статического электричества |
|---|---|---|
| 4 До хранения | 0,8 | 21 |
| 9 | 2,4 | 54 |
| 20 | 6,2 | 131 |

1) Duration of storage (days); 2) potential tars in fuel, mg/100 mk [sic]; 3) number of static-electricity discharges; 4) prior to storage.

Effect of Irradiation of JP-4 Jet Fuel

It has been established by research that the irradiation of JP-4 jet fuel with ultraviolet as well as gamma rays brings about an accel-

TABLE 235

Effect of Ultraviolet Irradiation of Fuel on the Formation of Static Electricity During Pumping (10 min.)

| 1 Образцы реактивного топлива JP-4 | 2 До облучения | | 3 После облучения | |
|---|---|---|---|---|
| | 4 число разрядов статического электричества | потенциальные смолы, мг/100 мл | число разрядов статического электричества | потенциальные смолы, мг/100 мл |
| A | 4 | 0,4 | 25 | 7,4 |
| B | 27 | 0,4 | 46 | 6,0 |
| C | 71 | 0,4 | 132 | 16,4 |

1) JP-4 jet fuel specimens; 2) prior to irradiation; 3) after irradiation; 4) number of static-electricity discharges; 5) potential tars, mg/100 ml.

ration of the fuel-oxidation process; in this case, there is a pronounced increase in the content of potential tars in the fuel.

In almost all cases of fuel irradiation with ultraviolet rays, the formation of static electricity increases during the pumping of this fuel (Table 235).

When a fuel is irradiated with ultraviolet rays, not only do we find an increase in the content of potential tars, but a sediment of about 0.5% is formed. Below we present the composition and quantity of sediment (% by weight) which forms in JP-4 jet fuel which has been irradiated with ultraviolet rays.

| | |
|---|---|
| Carbon | 57.32 |
| Hydrogen | 6.60 |
| Oxygen | 24.19 |
| Sulfur | 5.07 |
| Nitrogen | 3.59 |
| Ash | 3.03 |

The irradiation of the JP-4 jet fuel with gamma rays also significantly increases the formation of static electricity during the pumping of the fuel (Table 236).

TABLE 236

Effect of Irradiation of Jet Fuel with Gamma Rays on the Formation of Static Electricity

| 1 Образцы топлива JP-4 | 2 До облучения | | 3 После облучения | |
|---|---|---|---|---|
| | 4 число разрядов статического электричества | 5 потенциальные смолы, мг/100 мл | число разрядов статического электричества | потенциальные смолы, мг/100 мл |
| 1 | 8 | 1,0 | 113 | 17,0 |
| 2 | 18 | 0,4 | 81 | 13,6 |

1) JP-4 fuel specimens; 2) prior to irradiation; 3) after irradiation; 4) number of static-electricity discharges; 5) potential tars, mg/100 ml.

As has already been shown above, all light petroleum products in pure form have a specific electrical conductivity below $10^{-12}$ $ohm^{-1} \cdot cm^{-1}$ and under certain conditions exhibit the capacity to form a charge of static electricity. It has been established experimentally

that with an increase in the electrical conductivity of the fuels above $10^{-11}$ $ohm^{-1}$ $cm^{-1}$ the danger of static-electricity formation during operations with the fuel is markedly reduced.

It is on exactly this phenomenon that we base the proposed method of controlling the formation of static-electricity charges in fuels through the addition of special additives.

It has been noted that the introduction of a negligible quantity of certain substances such as, for example, acids, alkalis, and alkali salts to a fuel significantly increases its electrical conductivity. It has also been noted that the greatest effect is produced by those additives exhibiting high surface activity.

For example, the petroleum company "Royal Dutch Shell Company" has experimented with the utilization of the additive "Sa-Aerosol OT" to control the formation of static electricity during warehouse operations. However, the method of preventing the formation of static electricity in fuels by means of additives has not yet passed beyond the stage of laboratory and operational tests.

We know from the literature that in view of a number of specific conditions the formation of static electricity in a fuel is particularly likely during operations at the petroleum storage areas at airports and during the fueling of aircraft. It is precisely here that the latest equipment is employed, as well as fast pumping speeds and fine fuel filtration, i.e., favorable conditions are provided for the appearance of a great charge of static electricity.

To eliminate the danger of explosion and fire the petroleum company "British Petroleum Company," servicing the civil aviation of Great Britain, recommends the observation of the following rules during fueling of passenger aircraft.

1. Prior to start of aircraft fueling or removal of fuel from

aircraft tanks, the aircraft and all fueling devices must be properly and tightly attached to one another and grounded.

2. During aircraft fueling, with the passage of the fuel through the fuel system, the flexible hose, and the fueling nozzle, static electricity appears. To remove this charge of static electricity the flexible hose must be enclosed in a metal spiral and the manifold, hose, and fuel nozzle must be connected and grounded.

3. The tank of the fuel truck, the pump, the flowmeter, and the manifold must be reliably connected by copper wires to a chassis through which they are grounded.

4. The flexible hoses and the fuel nozzles must be reliably connected to the airplane being fueled prior to the start of fueling and this must be accomplished by means of special wires and plugs.

5. All connections and contacts on fuel trucks intended for the removal of static electricity must be carefully checked each and every day prior to start of operations.

6. Special points for the grounding of aircraft, fuel trucks, hoses, and tow trucks must be provided on an airfield at the points of aircraft fueling. The grounding points must be positioned so as to be easily accessible; they must be available in sufficient numbers.

7. All aircraft-fueling operations or all operations involving the removal of fuel from aircraft tanks must be brought to a halt when a storm is close to the airport or actually over it.

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[Footnote]

941 Paper entitled "Minimal'nyye temperatury samovosplameneniya goryuchikh veshchestv" [Minimum Autoignition Temperatures of Combustible Substances].

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script
Page
No.

[List of Transliterated Symbols]

938 т.в = t.v = temperatura vspyshk = flash point

938 т = t = toplivo = fuel

938 ат = at = atmosfernyy = atomospheric

940 TEC = TES = tetraetilsvinets = tetraethyl lead

## Chapter 30

## TOXICITY OF FUELS AND OXIDIZERS

All motor fuels are toxic to some extent, and because of failure to apply the required measures of care and safety in handling such fuels, they represent a certain danger to health and even life.

Poisoning may result if a fuel enters the human organism:

1) through the respiratory tract (inhalation of vapors);

2) through the gastrointestinal tract (swallowing);

3) through the skin;

4) through the mucous membrane of the eyes (in liquid or vapor state).

Poisoning through the respiratory tract is most dangerous, first of all, because of the great intake surface of the lungs (about 90 $m^2$ in an adult) and, secondly, because of the ease with which the poisons can pass through the lung alveolae into the circulation system. The poison acts almost 20 times more rapidly through the respiratory tract than it does through the gastrointestinal tract.

Only those toxic substances which are soluble in fats and the fatty substances of the organism can pass through the integument into an organism.

The danger of poisoning increases with a rise in the temperature of the ambient air, since in this case the evaporation of fuel is accelerated (the concentration of fuel in the air being inhaled is increased), the respiration rate increases, the cutaneous vessels expand, and there is pronounced penetration of the fuel into the organism.

Therefore, cases of poisoning are more frequent in the summer than in the winter.

The poisonous effect of a fuel also depends on the individual features of the human organism. People who have just recently recovered from a disease or who suffer from chronic diseases of the nervous system, the liver, kidneys, or the blood are particularly sensitive to the effect of poisons.

We distinguish two types of poisoning – acute and chronic. Acute poisoning involves the development of poisoning symptoms within several seconds – the lightning form – to many hours after the toxic dose of poison has begun to take effect. Chronic poisoning involves poisoning which develops as a result of the prolonged action of low concentrations of toxic substances, generally producing no poisoning symptoms if inhaled only once, even after a period of several hours.

THE TOXICITY OF GASOLINES

Vapor poisoning is most commonly encountered in the handling of gasoline.

The maximum permissible concentration of gasoline-solvent vapors in air is 0.3 mg/l, and in the case of motor gasoline (cracking, etc.) the maximum is 0.1 mg/l [5]. At higher concentrations, both acute and chronic poisoning may occur.

Acute Poisoning

Because of its high volatility, gasoline evaporates particularly rapidly. Therefore, if an open gasoline container were left in a closed or poorly ventilated enclosure or if the gasoline were to be poured and redistributed in various containers in this enclosure, the surrounding air would rapidly become saturated with the gasoline vapors and the concentration of these vapors in the air would, within a short period of time, perhaps become dangerous to human life. A con-

centration of vapors (from any gasoline) of 35-40 mg/l in the air is regarded dangerous for human life when inhaled for 5 to 10 minutes [1]. The inhalation of air containing lower concentrations will not immediately produce poisoning. Within a very few minutes after air containing a gasoline concentration of 5 to 10 mg/l the individual will begin to suffer from a headache, experience unpleasant sensations in the throat, coughing, and irritation of the mucous membrane in the nose and eyes. A longer stay in such an atmosphere, as well as an increase in the gasoline-vapor concentration, will result in more pronounced poisoning phenomena, instability of gait sets in, as do dizziness, weakness, stimulation similar to alcohol intoxication, dryness of mouth, and nausea; if the victim is not immediately removed, loss of consciousness, serious cramps, dilation of pupils, and respiratory weakness (possibly stopping entirely) set in.

Effect of Internal Consumption

Poisoning may also occur if the gasoline is taken internally. This is most frequently encountered when drivers draw gasoline into their mouths through siphoning hoses; it is found much less frequently as a result of gasoline being mistaken for a potable liquid. Such "consumption" of gasoline internally frequently results in serious illness - inflammation of the lungs (pneumonia).

Chronic Poisoning

Chronic poisoning by gasoline vapors occurs when vapor concentrations in excess of the maximum permissible limits are encountered on a regular basis. The basic symptoms of chronic poisoning are headache, lethargy, tendency to become easily tired, loss in weight, irritability, drowsiness, or insomnia.

Chronic inflammation of the mucous membrane of the eyes, more frequent respiratory-tract diseases, etc., may be the result of the

action of gasoline vapors.

Effect on Skin

Gasoline can also produce a harmful local effect on contact with the skin. It stimulates the nerve endings of the skin, and this causes skin irritation (burns, itching), and expansion of blood vessels (reddening, edema). Since gasoline is a good solvent of fats, it dissolves the cutaneous fat. Deprived of its fat the skin dries out. Cracks form more easily on a dry skin, and such cracks provide fertile soil for the development of infections: pyoderma, eczema. Such diseases develop most frequently in gas-station attendants, drivers (chauffeurs), etc. If the body remains in contact for a prolonged period of time with a gasoline-soaked cloth, reddening of the skin sets in and blisters appear. Gasoline can penetrate the human organism through undamaged skin as well, but since no conditions prevail within the organism for the accumulation of gasoline, it is rapidly exhaled through the lungs. This property of gasoline must always be borne in mind, since various substances dissolved in the gasoline can penetrate through the undamaged skin to the human organism together with the gasoline; we have reference here to such substances as the antiknock additive tetraethyllead, which is capable, even in small quantities, of producing serious poisoning.

Preventive Measures

To prevent the possibility of poisoning in handling gasolines, the following is necessary.

1. In the enclosure in which motor fuel is being handled and in which elevated concentrations of motor-fuel vapors may occur, it is necessary to provide for fresh-air/exhaust ventilation with floor and ceiling exhaust.

2. In cleaning petroleum products out of, and in repairing, tank

cars and other storage containers they must first be thoroughly flushed with air or steam. All work of this type, involving an atmosphere with a high fuel-vapor content, must be carried out in the presence of a second individual (a safety man).

3. Workers called upon to work in an atmosphere with high concentrations of gasoline vapors must undergo preliminary and periodic medical examinations.

4. All workers periodically subjected to the effect of high concentrations of gasoline vapors must know how to offer first aid to an injured worker and how to perform artificial respiration.

5. To prevent skin irritations the workers must wear special clothing, wash their hands frequently with soap, and use protective salves.

6. On jobs (even of short duration) under conditions of high concentrations of gasoline vapors it is necessary to use hose-type PSh-1, PSh-2 gas masks, or the KIP-5 or RKR-3 oxygen devices.

7. If splashed to any significant degree with gasoline, it is necessary to remove clothing (replacing it or airing it until all traces of odor disappear) and take a hot shower.

First aid

If poisoning has occurred, the injured must first of all be removed (carried out) into the fresh air from the harmful atmosphere, and a doctor must be called.

Before the arrival of the doctor, if excitation should set in valerian drops should be administered. If respiration is markedly weak or faintness has set in, the injured should be given spirits of ammonia to smell and pure oxygen to inhale. In more serious cases, if breathing has stopped entirely, artificial respiration should immediately be undertaken and continued until (and this may sometimes take hours) in-

dependent breathing is restored. After the restoration of normal respiration the injured should be fed strong tea or coffee and removed to the closest hospital.

If the mucous membrane of the eyes should become irritated, it must be washed with a 2% soda solution or with pure water.

TOXICITY OF KEROSENE AND DIESEL FUEL

The poisonous effect of kerosene and diesel fuel is, for the most part, similar to the poisonous effect of gasoline. Exhibiting lower vaporizability, these products exert a less pronounced over-all effect on the human organism, but the irritating effect of kerosene and diesel fuel has a more pronounced effect (in vapor form) on the mucous membrane, and a more pronounced effect on the skin (in liquid form).

The maximum permissible concentration of kerosene and diesel-fuel vapors in the air is 0.3 mg/l [5].

Acute Poisoning

Phenomena of acute poisoning may develop on inhalation of large concentrations of kerosene and diesel-fuel vapors. Drowsiness, the tendency to tire easily, ringing in the ears, headaches, irritability, digestion disturbances, irritation of the upper respiratory tract, and sometimes burning in the eyes is noted in victims of this type of poisoning. However, when working in open air, as a rule, concentrations of vapors sufficient to produce poisoning are generally not encountered. Therefore, cases of acute poisoning as a result of kerosene and diesel-fuel vapors are encountered quite rarely.

Chronic Poisoning

Chronic poisoning due to kerosene and diesel-fuel vapors is encountered comparatively rarely.

In Reference [1] we find a description of cases in which, after prolonged work with kerosene (from 5 weeks to 3-4 years) the following

symptoms associated with chronic poisoning were established: headaches, loss of appetite, itching of skin on hands, pain near heart, emaciation, general weakness, insomnia, etc.

Effect on Skin

Kerosene, more frequently than gasoline, on coming into contact with the skin produces acute and chronic diseases of the cutaneous cover.

When a stream of kerosene under pressure strikes the fingers on a hand, pain and numbness set in during the first hours; after 2 to 3 hours, there is pronounced edema, and a minute opening forms at the point of stream contact. The sharp pain and edema last for 8 to 10 days. Mummification of the damaged tissue is possible.

The preventive measures and first aid are the same as in handling gasolines.

TOXICITY OF BENZENE

Benzene vapors are substantially more toxic than gasoline vapors. Benzene is, first of all, a nerve-cell poison. The prolonged action of benzene will produce the degeneration of the fatty tissue of internal organs, vascular walls, serious damage to the hematogenetic organs (bone marrow), reduced blood coagulation with increased vascular brittleness (bleeding from mucosae), and there is also a pronounced drop in the resistance of the organism to all types of infection.

The maximum permissible concentration of benzene vapors in air is 0.02 mg/l [5].

Acute Poisoning

Acute poisoning by benzene is possible when cleaning benzene from tanks, when using benzene in combination with fast-drying paints while working in poorly ventilated enclosures or in chemistry laboratories. In cases of slight poisoning, the victim suffers from headaches, red-

dening of the face, stimulation (similar to alcoholic intoxication), quickly replaced by paleness and dizziness.

Given a more prolonged exposure to benzene vapors or given an increased concentration of these vapors, loss of consciousness may occur.

In serious cases, loss of consciousness, respiratory impairment, and a drop in cardiac activity take place almost instantaneously; if no medical aid is available, death may occur.

Slight cases of benzene poisoning generally leave no trace. After serious poisoning, however, prolonged impairment of health is noted: (diseases of the central nervous system, the liver, and the lungs).

Chronic Poisoning

In actual practice, we encounter more frequently phenomena of chronic rather than acute benzene-vapor poisoning. This form of poisoning develops during extensive work with benzene, even under conditions of low benzene-vapor concentrations in the air. Chronic benzene poisoning results in numerous changes in almost all organs of the human organism.

Workers complain of over-all weakness, headaches, dizziness, and poor appetite. Sometimes the symptoms include bleeding gums, nosebleed, and petechial hemorrhages on the skin. Changes in the composition of the blood (reduced numbers of white blood cells, etc.) are quite characteristic of chronic benzene poisoning.

Effect on Skin

If benzene comes into contact with the skin frequently, pronounced irritation may result: reddening, itching, edema, blister rashes, eczema. The effect of benzene is more pronounced on the skin than is the effect of gasoline or kerosene. It has been demonstrated that benzene may be drawn into the organism through undamaged skin.

The preventive measures and first aid for acute cases of benzene

poisoning are, for the most part, the same as in work with gasoline.

Individuals called upon to work for prolonged periods with benzene must undergo medical examinations every 6 months and an analysis of the blood is mandatory. If changes in the blood are detected, these individuals must be transferred to other jobs which do not involve contact with benzene.

TOXICITY OF ETHYL FLUID

If not handled carefully, ethyl fluid represents great danger both from the standpoint of health and life. The most toxic component part of ethyl fluid is tetraethyllead.

Tetraethyllead is an extremely powerful poison. It penetrates easily into the organism through the respiratory organs, and is also easily drawn in through undamaged skin. Even an insignificantly small quantity of tetraethyllead, in the organism, can result in serious illnesses.

The maximum permissible concentration of TES [TEL – tetraethyllead] in the air is 0.000005 mg/l [5].

The danger in handling ethyl fluid is increased by the following.

1. Wood and other porous materials soak up ethyl fluid well. Wool, cotton, and linen clothing, as well as leather footwear, do not protect the body against liquid drops or vapors of ethyl fluid. Absorbing these, they can become sources of serious illnesses. In other words, all objects that come into contact with ethyl fluid become dangerous from the standpoint of health until such time as they are degassed.

2. If ethyl fluid comes into contact with the body there is no sensation of pain, burning, itching, nor is there any irritation of the eyes or the respiratory tract, thus producing the false impression that such contact with ethyl fluid has no harmful effect on one's

health.

3. Tetraethyllead exhibits the capacity to accumulate in the organism. Penetrating the organism in an insignificant quantity, tetraethyllead need not immediately affect the health of the individual, but rather at such time as the quantity of tetraethyl lead in the organism has increased to a certain limit as a result of new accumulations. This latent period may last anywhere from several hours to several days.

Cases of poisoning as a result of lead compounds have been observed in cases of inhalation of dust formed in the cleaning of an engine motor, and in cases of inhalation of scale formed after the operation of an engine on ethylated gasoline.

Acute Poisoning

Ethyl fluid causes serious impairment of the activity of the central nervous system. In the case of slight poisoning, there is a weakening of the pulse (less than 50 beats per minute), a drop in body temperature, as well as a drop in arterial pressure.

Acute poisoning results in violent reactions. The victim is extremely excited, suffers from visual and aural hallucinations, becomes excessively talkative, refuses food, cannot fall asleep, becomes aggressive, exhibits suicidal tendencies, and develops complexes of persecution and guilt. Acute poisoning may end in the death of the victim within the first few hours after the poisoning, or after 3 to 5 days or more.

We know of the following case of serious poisoning [6]. Troops from a particular German army unit assumed a barrel containing ethyl fluid (without markings) to be paint. After several hours of painting the walls of their barracks, 21 soldiers showed signs of tetraethyllead poisoning and acute toxic psychosis. The majority of the victims

died.

Serious cases of poisoning resulting in death are even possible in everyday life when using items contaminated with ethyl fluid. For example [6], a worker picked up a rubber hose from a factory dump and took it home. As a result, each of the six people living in the room with this worker showed signs of tetraethyllead poisoning. After several days an 11-year old girl and a 17-year old youth died. The neighbors suffered slight cases of ethyl-fluid poisoning. The investigation revealed that the rubber hose had been used at the gasoline-mixing station where it was employed for pumping of ethyl fluid.

Chronic Poisoning

Acute cases of poisoning are extremely rare. Chronic cases of ethyl-fluid poisoning are encountered much more frequently. Given the regular action of small quantities of ethyl fluid, chronic poisoning may set in.

Patients express similar complaints in cases of both acute and chronic poisoning. In the latter case, these complaints are not as serious. The victims are disturbed by headaches, dizziness, impairment of memory, insomnia, nightmares, increased salivation, general weakness, "bitterness in the mouth," nausea, etc.

Cases of chronic poisoning occur generally when working in a zone of increased TES [TEL] vapor concentrations (from 0.0007 to 0.002 mg/l).

Preventive Measures

In working with ethyl fluid it is absolutely necessary to use a filtering A (MKhP, 1951) gas mask and special clothing (a rubber suit, overalls, gloves, shoes). After each 30 hours of use, the gas mask should be replaced. It is necessary to take the following preventive measures, intended to provide such industrial (laboratory) conditions

as would exclude the possibility of the liberation and accumulation of ethyl fluid and its oxidation products in the work areas.

1. Ethyl fluid and gasoline should be mixed only in installations and areas specially designated for this purpose.

2. It is forbidden to remove ethyl-fluid contaminated items (containers, hoses, work clothing) from the area of gasoline-mixing stations and ethyl-fluid storage areas.

3. Buildings in which work with ethyl fluid is carried out must be equipped with appropriate fresh-air/exhaust ventilation devices.

4. In laboratories, work with ethyl fluid should be carried out exclusively beneath an exhaust hood.

5. Degasification means should always be available in the vicinity of areas in which work is being done with ethyl fluid (kerosene, a 3% solution of chloramine, bleaching powder, etc.).

6. All work areas should be degasified periodically.

7. Workers who come into contact with ethyl fluid must be provided with special work clothing (desirably, coated coveralls), gas masks and similar means of personal protection, each accompanied by appropriate instructions.

8. All workers should be trained in safety measures.

9. All workers who come into contact with ethyl fluid must be subjected to preliminary and periodic (once every 3 months) medical examinations.

10. People younger than 18 years should not be permitted to work with ethyl fluid.

11. It is recommended that individuals working with ethyl fluid be periodically assigned to jobs which do not involve contact with ethyl fluid.

Acute cases of poisoning can be prevented even after an individual

has been doused with a substantial quantity of ethyl fluid, if immediately (within the first minutes) after contact of the ethyl fluid with exposed portions of the body all clothing is removed, the injured sections treated with kerosene, and the body surface carefully washed with hot water and soap.

Decontamination Procedures

All items and materials contaminated with ethyl fluid are decontaminated:

a) with solvents (kerosene, nonethylated gasoline, dichloroethane);

b) decomposition with chloramine, dichloramine, and bleaching powder.

Cotton-fabric products and special work clothing should be decontaminated in one of the following ways:

1) by placing them into a special chamber with hot steam, for 45 to 60 minutes, at 110-120° and a pressure of 2 atm;

2) soaking for 2 hours in kerosene, with subsequent boiling and rinsing in a hot 1% solution of monochloramine;

3) airing in fresh air for 2 to 3 hours, with subsequent washing in a 1% solution of monochloramine.

Rubber boots and gloves are covered for 1 hour by a layer of bleaching-powder paste, after which each item is washed in hot water with a soapy sponge.

When ethyl fluid comes into contact with wood, rubber, concrete, stone, or soil (even in small quantities), the following should be used for purposes of degasification: chlorine water, a bleaching-powder paste ($CaOCl_2$), and water (1 part bleaching powder for each 3-5 parts of water) or a 5% solution of sulfuryl chloride ($SO_2Cl_2$) in kerosene.

The bleaching powder and the sulfuryl chloride, in dry form, in-

teract vigorously with ethyl fluid, and there is great liberation of heat, as a result of which the ethyl fluid ignites. Therefore, these can be used only in dilute form.

Prior to degasification, the spilled ethyl fluid must be cleaned up with shavings or sand, and then the spot that was doused with the ethyl fluid must be treated with a chemical reagent. The shavings and sand, soaked with the ethyl fluid, are doused with a combustible and burned.

After treatment with the degasifier, the affected spot is washed with water and then with a soapy solution. When ethyl fluid is spilled on soil, the contaminated section, after degasification, should be spade-turned 2 to 3 times, to a depth of 0.5 meter.

First Aid

If ethyl fluid should come into contact with clothing, the latter must immediately be removed and the body skin must be washed at the appropriate point. If ethyl fluid should be taken internally, vomiting should be induced immediately. Those portions of body skin that have come into contact with the ethyl fluid should immediately be treated (2 to 3 times) with cotton soaked in kerosene or unethylated gasoline, and then thoroughly washed with hot water and soap. After the first premedical aid, the victim must be brought to the nearest hospital.

TOXICITY OF ETHYLATED GASOLINE

More than 35 years of experience in the extensive utilization of ethylated gasolines and extensive investigations of their effect on the human organism offer convincing proof of the fact that ethylated gasoline, in terms of harmful effect, differs but slightly from ordinary gasoline, if the elementary rules of safety are observed when this material is used. For example, Lind [6] in his examinations, in

1934 of 215 workers who had come into contact with ethylated gasoline in the course of a year, found not a single symptom of lead poisoning. Of those who were examined, 107 workers were employed at the tanks, there were 61 mechanics, 47 drivers carrying gasoline tanks, and 48 drivers working directly with ethylated gasoline.

The weak toxicity of ethylated gasolines, despite the fact that they contain up to 4 ml of ethyl fluid, can be explained by the fact that in the majority of cases the vapors of these ethylated gasolines do not differ at all (in terms of toxicity) from vapors of conventional gasolines, since during the evaporation of up to 30% of the ethylated gasoline all of the tetraethyllead remains in the liquid gasoline. Only in the case of further gasoline evaporation does the tetraethyllead gradually vaporize together with it. During drainage, fueling, and storage of ethylated gasoline, when there is occasion to breathe its vapors, the evaporated part of the gasoline, in the very worst of cases, amounts only to several percent of the total quantity and, therefore, there is no TES [TEL] contained in the vapors.

Ethylated gasolines are dangerous in the following cases:

a) during the cleaning and repair of containers which held ethylated gasoline;

b) during the repair of engines operating on an ethylated gasoline;

c) in the case of extremely frequent contact of ethylated gasoline with the body and clothing, and in the case of its accidental internal consumption;

d) when ethylated gasoline is spilled over a large surface, particularly under the conditions prevailing in a closed poorly-ventilated building.

Let us examine each of the above-cited cases individually.

When storing ethylated gasoline for long periods of time, up to 15% oxidized TES [TEL] may settle out. Consequently, after the ethylated gasolines are drained out, a substantial quantity of toxic TES [TEL]-decomposition products may remain at the bottom of the container in the form of a residue. Therefore, in cleaning tank cars and other storage containers of ethylated gasolines, safety measures must be implemented.

Kassel's and Dodds [sic] [1] describe the following case, which happened in Great Britain. A group of workers was assigned to the task of cleaning an ethylated-gasoline storage tank. However, the required preventive measures (complete change of regular clothing for special work clothing, rubber aprons, rubber gloves and boots, showering upon completion of work, flexible-hose gas mask, etc.) were not put into effect, and as a result there were 25 cases of acute TES [TEL] poisoning, and two cases resulted in the death of the victim.

A cause of lead poisoning may be improper handling of scale and sedimentation formed in engines operating on ethylated gasoline. Here we should take into consideration that scale and sedimentation form in the cylinders, the exhaust pipes, and other parts of motors, and this scale and sedimentation contain up to 45% and more of lead compounds.

In actual practice we encounter most frequently cases in which ethylated gasolines come into contact with the human body and clothing.

The tetraethyllead contained in ethylated gasolines rapidly enters the organism both through cuts as well as through skin that is completely intact [1, 6], without producing any external changes or unpleasant sensations. In these cases, an extremely small quantity of tetraethyllead enters the organism. If dousing with ethylated gasoline occurs comparatively infrequently and involves only insignificant quan-

tities, there are no particularly harmful consequences, since the tetraethyllead disintegrates into its component parts in the human organism and is carried out with the urine, fecal matter, and perspiration. However, if dousing with ethylated gasoline is a frequent occurrence, the quantity of tetraethyllead that penetrates the organism may sometimes exceed the quantity carried out of the organism. In these cases, the protective functions of the organism prove to be inadequate, and symptoms of chronic poisoning develop.

The early symptoms of chronic poisoning are frequently so unspecific that they may easily be overlooked. They are expressed in quickness to tire, certain barely noticeable changes in character, instances of alienation, and frequent nosebleeds. When careless handling of ethylated gasolines has been going on for a long time, symptoms of damage to the central nervous system become clear. In such cases the patients complain of headaches (the sensation of a "weight" in one's head), disturbed sleep, loss in weight. They fall asleep with difficulty, and once asleep, frequently wake up, and their bodies jerk during sleep. Sleep is restless, many dreams, some pleasant, mostly nightmares.

If the basic rules of hygiene and safety are observed work with ethylated gasolines is completely safe.

Personal Hygiene and Preventive Measures

In working with an ethylated gasoline the following rules should be observed [1, 2].

1. Ethylated gasoline should be used only as a motor fuel; under no circumstances should it be used to wash hands, machine parts, or to clean clothing, etc.

2. Before meals hands and face must be washed with warm water and soap. Eating, drinking, and smoking is strictly forbidden in buildings

in which ethylated gasoline is being poured and in which component parts of motors operating on ethylated gasoline are being repaired.

3. All people assigned to jobs involving the use of ethylated gasoline must be subjected to a preliminary medical examination and must undergo periodic medical check-ups each 6 months.

4. If ethylated gasoline should be spilled in a closed building, the spot should immediately be wiped with a dry rag, and then with a rag soaked in kerosene.

5. If ethylated gasoline should come into contact with clothing, the clothing must be removed and aired in fresh air until all traces of a gasoline odor disappear.

6. If ethylated gasoline should come into contact with the skin, the gasoline should not be permitted to dry out; the sections of skin over which the gasoline spilled should immediately be washed with pure gasoline or kerosene, and if these are not available the section should be wiped with a clean rag and then washed with warm water and soap.

7. All barrels, tank cars, and storage tanks containing ethylated gasoline must be clearly marked "ethylated gasoline"; it is forbidden to take the work clothing home; arrangements for the laundering of this special work clothing must be made at the job.

8. If the gasoline fuel lines or the carburetor jets become fouled, they should be flushed only with a pump or a hand spray, but under no circumstances orally; cleaning and flushing of component parts must be carried out in rubber, polyvinylchloride, or leather gloves.

9. Repair and overhauling of motors operating on ethylated gasolines must be carried out under the supervision of individuals responsible for the implementation of safety measures. Such jobs must be preceded by the flushing of the system with nonethylated gasoline in

order to remove tetraethyllead residues.

10. An individual will be permitted to work with ethylated gasoline only after he has passed the minimum sanitary-technical requirements.

## TOXICITY OF EXHAUST GASES

Exhaust gases from internal-combustion engines, depending on the type of engine, the type of fuel, and the operating regime, consist of 1-9% CO, 2-10% $CO_2$, 0.5-5% $O_2$, 0.5-8% saturated hydrocarbons, up to 0.5% unsaturated hydrocarbons, 1-7% $H_2$, and 69-79% $N_2$. Of all the component parts of exhaust gases, the carbon monoxide is the most dangerous.

If an engine is operating in a garage or in some other closed building, particularly if there is limited space, and also if the exhaust system is not functioning properly, a dangerous concentration (for a human being) of carbon monoxide may form.

The maximum permissible concentration of carbon monoxide in air is 0.02 mg/l [5]. For example, a 20 hp engine can produce 28 liters of carbon monoxide in only a single minute, and if the doors of a one-car garage are closed, a lethal concentration accumulates within 5 minutes.

### The Nature of the Effect

Carbon monoxide is one of the most dangerous of poisons. Its affinity with hemoglobin is greater than that of oxygen by a factor of 300. Entering the blood through the lungs, carbon monoxide combines easily with the hemoglobin of the blood, forcing out the oxygen. The blood loses its ability to supply the required life-giving oxygen to the tissue, as a result of which anoxia (oxygen starvation) sets in. In addition, carbon monoxide exerts a direct poisonous effect on the central nervous system.

Acute Poisoning

The basic symptoms of acute poisoning are the same as in the case of charcoal-smoke poisoning: a sensation of forehead compression, strong pain in forehead and temples, unsteadiness of vision, pulsation in temples and ringing in ears, and tendency to tire easily upon physical exertion. With a continued stay in such an atmosphere, mental confusion, nausea, symptoms similar to alcoholic intoxication, weakness in the legs, lowered arterial pressure, loss of sensation, and impairment of memory set in, the cutaneous cover and the mucous lining turn pink, and finally there are cramps and loss of consciousness. The victim may remain in a state of unconsciousness for 1 to 2 days, but if the concentration was particularly great death will come almost instantaneously.

The central nervous system is particularly sensitive to CO poisoning. In the case of serious poisoning, symptoms include impairment of hearing, olfaction, and taste. Quite frequently paralysis sets in.

Acute CO poisoning is frequently complicated by various disturbances due to the central nervous system, a disease of the thyroid gland, changes in the kidneys, the suprarenal glands, gastrointestinal disturbances, and reduced resistance of the organism to infections. Young people, pregnant women, and alcoholics are particularly sensitive to the effect of CO. Slight indications of poisoning appear upon inhalation of a concentration of CO of 0.23 mg/l for a period of more than 5 hours (headache, which quickly disappears in fresh air).

At a concentration of 0.34 mg/l the first indications of poisoning appear within 4 hours. A concentration of 0.46 mg/l will produce extreme occipital and frontal headaches within one hour; a concentration of 1.34 mg/l will induce palpitation within 33 minutes; after 1.5 hours the symptoms include light rocking, difficulty in breathing;

after 2 hours, blurred consciousness. At a concentration of 3.4 mg/l death takes place after several inhalations [1].

Chronic Poisoning

The prolonged inhalation of air containing carbon monoxide in small concentrations may, with the passage of time, result in chronic poisoning, accompanied with the development of headaches, dizziness, loss of weight, as well as increased irritability, indifference, and obsessive fear.

Preventive Measures

Good ventilation must be provided and regular monitoring of the carbon-monoxide content in the air must be carried out in those sections in which increased concentrations of carbon monoxide may be liberated and accumulate during the course of work. When working in an atmosphere with an increased concentration of carbon monoxide, it is recommended that a M (MKhP, 1951) brand filtering gas mask be used; in the case of high CO concentrations only the filtering KIP-5 and RKR-3 (regeneration oxygen respirators) should be used. To prevent the entry of exhaust gases, the equipment and fuel systems must be hermetically sealed, and the ventilation must function normally.

If it is necessary to work no longer than one hour in an atmosphere containing carbon monoxide, the maximum permissible concentration of carbon monoxide should not be higher than 0.05 mg/l; if the working time is below 30 minutes, the concentration should not exceed 0.1 mg/l; if the working time is shorter than 15 minutes (garage pits), the concentration should not exceed 0.2 mg/l.

Repeated work under conditions of elevated carbon-monoxide content in the air in the work zone may be permitted with breaks lasting no less than 2 hours.

First Aid

In case of poisoning quickly put a gas mask on the victim, after which it is absolutely necessary to carry him out into the fresh air and, having taken measures to prevent possible drafts (covering him, etc.), begin to apply artificial respiration and try to get him to breathe pure oxygen, or better yet, pure oxygen mixed with 5-7% carbon dioxide in order to increase the respiratory volume.

If breathing has stopped entirely, artificial respiration must be continued until signs of life reappear, even if this involves several hours, and the artificial respiration must be continued all the way to the hospital.

TOXICITY OF OXIDIZERS

Concentrated nitric acid $HNO_3$, saturated with oxides of nitrogen (NO, $NO_2$, etc.), concentrated hydrogen peroxide $H_2O_2$, liquid oxygen $O_2$, tetranitromethane $C(NO_2)_4$, etc., are the most commonly used oxidizers. All of the above-enumerated oxidizers are toxic to some extent and they may serve as sources of serious poisoning if the rules for their handling are violated.

Toxicity of Concentrated Nitric Acid Saturated with Nitrogen Oxides

Nitric acid saturated with nitrogen oxides is a powerful oxidizer. In combination with many organic substances such as, for example, analine, xylidine, and furfuryl alcohol, concentrated nitric acid reacts with an explosion. Its utilization as a rocket propellant component is based on this property. Organic materials (straw, wood, etc.) as well as clothing will burst into flame when doused with nitric acid. When nitric acid comes into contact with metals, organic substances, or in reaction with oxygen, the acid decomposes with the formation of the oxides. The most toxic of the nitrogen oxides are nitrogen dioxide and tetroxide.

The vapors released by nitric acid irritate the upper respiratory tract (produce coughing, choking, difficulty in breathing, and they irritate the mucous membrane). Nitrogen oxides liberated from nitric acid are not often found in the upper and middle sections of the respiratory tract because of their poor solubility, but they have more serious effects on deeper sections of the respiratory organs – the bronchioles and the alveolae. In combination with the moisture in the organism, these nitrogen oxides form nitric and nitrous acids which produce a variety of inflammatory manifestations in the mucous membranes of the respiratory tract (bronchitis and even toxic edema of the lungs).

One of the oxides of nitrogen (NO) is a blood poison which disrupts the supply of oxygen to the tissues by the blood and damages the central nervous system. Poisoning caused by pure nitrogen oxide (NO) is rare, since it is rapidly oxidized by the oxygen of the air into nitrogen dioxide.

The maximum permissible concentration of nitrogen oxides in the air is 0.005 mg/l when calculated for $N_2O_5$ in accordance with the norm (N101-54). At higher concentrations acute [6] and chronic poisoning occur.

Acute Poisoning

Acute poisoning by nitric-acid vapors and vapors of nitrogen oxides depends on the combination in which the individual ingredients appear. Generally, poisoning begins with the irritation of the upper respiratory tract (coughing) and the mucous membrane of the eyes. After 15 to 30 minutes, the degree of irritation diminishes and the patients feel quite well. But within 4 to 6 hours after the completion of the "latent period," i.e., after the seeming well-being of the patient, there sometimes develops a violent pattern of toxic edema of the lungs

and the victim perishes.

In other cases of severe poisoning, upon completion of the latent period, there appears a sensation of chest compression, harsh coughing (spasmatic), frequently with blood, body temperature rises, breathing becomes difficult, and the cutaneous cover turns blue. In this case we frequently observe a disturbance of the gastrointestinal tract (nausea, vomiting, and diarrhea). If the illness follows its normal course, the above-mentioned symptoms of toxic edema of the lungs abate by the 5-th to 7-th day. These illnesses are frequently complicated by inflammation of the lungs. The treatment of severe poisoning cases requires anywhere from 2 to 6 weeks.

In light cases, the time lost from work ranges between 3 and 5 days [4].

According to the data of Alyavdin [4], the inhalation of air with a concentration of 0.15 mg/l of nitrogen oxides for a period of 4 minutes will induce choking, repeated coughing, and irritation of the throat. Inhalation of air for 5 minutes with a concentration of 0.09 mg/l of oxides will produce severe irritation of the pharynx, coughing seizures, salivary discharge, and at 0.02 mg/l there will be a definite odor; at 0.01 mg/l, the odor will barely be perceptible; at 0.003 mg/l no harmful effect is observed. A daily 8-hour stay in an atmosphere with a nitrogen-oxide concentration not exceeding 0.000005 mg/l is regarded as harmless.

All of these harmful effects quickly disappear in fresh air.

Chronic Poisoning

In the case of elevated nitrogen-oxide concentrations (above the permissible limits) for extended and regular periods, chronic inflammatory diseases of the mucosae of the upper respiratory tract develop, as does chronic bronchitis, emphysema, tooth decay, and there is a dis-

ruption of the metabolism. Sometimes we also observe the ulceration of the mucous membrane of the nose or mouth.

Effect on the Skin

If concentrated $HNO_3$ should come into contact with the skin it will produce severe burns requiring extensive treatment. Dilute solutions of $HNO_3$ may be responsible for the development of chronic eczema. High concentrations of nitrogen-oxide vapors sometimes cause hair to yellow, as well as the yellowing of nostrils and hands.

Preventive Measures

The preventive measures are the same as in the case of work with other toxic volatile substances - hermetic sealing of the equipment in which vapors of $HNO_3$ and nitrogen-oxide vapors can form or be liberated, as well as the installation of an appropriate exhaust system.

People suffering from bronchitis, asthma, or heart disease should not be permitted to work with nitrogen oxides; people working in an atmosphere containing high concentrations of nitrogen-oxide vapors must be provided with gloves, aprons, and protective goggles and individual oxygen masks.

Care should be taken that the gloves should not be damaged in any way, i.e., there should be no tears or punctures. If acid should be spilled on the floor it would liberate nitrogen oxides which could result in serious poisoning. The spilled acid must be neutralized with a soda or lime solution and washed away with water. To protect against nitrogen oxides and $HNO_3$ vapors, we use the filtering "B" brand gas mask (the yellow box).

First Aid

The victim must be removed from the harmful atmosphere quickly and he must immediately be transferred to a hospital in a supine position. Prior to sending the victim to the hospital, he must be made to

lie down, kept completely quiet, given pure oxygen to breathe, and after all pieces of tight clothing have been loosened, he should be packed in hot-water bottles.

If nitric acid should come into contact with the skin the injured spot should be washed immediately with a large quantity of water and treated with a 2% solution of drinking soda, after which the spot should be smeared with vaseline. In case of injury to the eyes, a heavy stream of water should be directed at the eyes for a period of 15 minutes and more, and then the eyes should be washed out with a 1-2% solution of soda.

Should nitric acid come into contact with the inside of the mouth, the mouth should be rinsed with water and then with a 3-5% solution of soda. If the $HNO_3$ should be taken internally, as much water as possible should be taken and vomiting should be induced. Even when the initial symptoms of poisoning do not seem dangerous, the victim should nevertheless be kept in bed for 24 hours.

Toxicity of Concentrated Hydrogen Peroxide

Concentrated hydrogen peroxide ($H_2O_2$), in contact with organic materials (wood, clothing, paper, etc.), causes these to ignite. Concentrated hydrogen peroxide produces an explosion on mixing with combustible substances.

Contamination of concentrated hydrogen peroxide by dust, alkalis, most metals and their oxides, as well as by many other substances of the most diverse origins, can result in the violent decomposition of the peroxide. This decomposition takes place with the liberation of gases and heat adequate for the ignition of the combustible materials nearby, and the explosion of the container if the gases being liberated do not find a free exit.

The maximum permissible concentration of concentrated $H_2O_2$ vapors

is held by a number of authors [10] to be 0.004%. Concentrated $H_2O_2$ not only irritates the mucous membrane of the eyes and the respiratory tract (tearing, hoarseness, scratching, and the sensation of a metallic taste, a cold, and substantial discharge of sputum), but it also exhibits general toxic effects. The prolonged action of hydrogen-peroxide vapors destroys tissue. Given daily prolonged (up to several hours) work under conditions in which elevated concentrations of concentrated hydrogen-peroxide vapors are in action may result in damage to the central nervous system (headaches, tendency to tire easily, drowsiness). If hydrogen peroxide comes into contact with the skin for a short period of time, it produces bleaching and the sensation of a burn, which rapidly disappears. The prolonged action of hydrogen peroxide on the skin will result in serious burns.

Preventive Measures

The building in which work with concentrated $H_2O_2$ is being done must be equipped with fresh-air/exhaust ventilation; the floors must be made of a moisture-proof material (ceramic plates, cement) and must be slanted to make possible the rapid washing away of spilled concentrated $H_2O_2$. Workers who have come into contact with concentrated $H_2O_2$ must wear goggles, special work clothing (desirably, made of airtight "textavinite") and polyvinylchloride gloves.

Treatment

With the appearance of poisoning symptoms (irritation of mucous membrane, headaches) the victims must be removed from the zone of injury into fresh air and be sent to hospitals for the required specialized medical assistance. If concentrated $H_2O_2$ should come into contact with the skin, that portion of the skin must immediately be washed with a liberal quantity of water.

Toxicity of Tetranitromethane

Tetranitromethane vapors have an irritating effect on the respiratory tract and on the mucous membranes of the eyes. The basic symptom of this type of poisoning is [11] pronounced salivation with subsequent inflammation of the respiratory tract.

Given frequent and prolonged exposure to elevated concentrations of tetranitromethane vapors, symptoms of chronic poisoning with injury to the central nervous system may appear (headaches, tendency to tire rapidly, weakness), as well as injury to the cardiovascular system, and also symptoms of anemia. The above-enumerated symptoms of poisoning may also include digestive disturbances (loss of appetite, heartburn, vomiting).

In most severe cases, which sometimes result in the death of the victim as a result of developing edema of the lungs, yellowing of the cutaneous covers and sclerae was observed.

In the case of insignificant concentrations, slight irritation occurred immediately after the removal of the victim from the poison atmosphere. The sensitivity of individuals to tetranitromethane depends on the individual characteristics of the person involved. The maximum permissible concentration of tetranitromethane vapors is 0.0003 mg/l [5].

First aid

Upon the appearance of poisoning symptoms it is necessary to remove the victim from the injurious atmosphere and send him immediately to a hospital.

Toxicity of Liquid Oxygen

Pure gaseous oxygen is not poisonous. When inhaled for short periods of time it has no harmful effect on the human organism. The danger to human health arises only in the case of liquid oxygen coming

into contact with the skin. In this case limited (of short duration) contact between the skin and liquid oxygen involves no harmful consequences because a protective gas layer is formed between the skin and the liquid oxygen. However, prolonged contact between skin and liquid oxygen produces serious burns.

Preventive Measures

In work with liquid oxygen it is necessary:

a) to use gloves and protective clothing;

b) to make certain that all connections, component parts, and manifolds have been thoroughly degreased at all installations in which liquid oxygen is handled;

c) to make certain that no flames or hypergolic substances are permitted in the vicinity of liquid oxygen.

It is important to bear in mind that in an oxygen atmosphere woolen and cotton materials can ignite.

Treatment

Burns resulting from liquid oxygen are treated in the same way as conventional burns.

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