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THE CHEMISTRY OF REACTION FUELS

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FOREWORD

During the past 15 to 20 years, reaction-thrust (rocket) engineering has undergone particularly rapid development.

The engines which are used in reaction-thrust flying craft operate on the principle of the reaction of a stream of gases, formed in the burning of a propellant, said gases being discharged through an open nozzle section at a great velocity.

We know of two types of engines: there are air-reaction engines and there are rocket engines. In the case of air-reaction engines, petroleum products serve as the combustible (fuel) and the oxygen of the air is employed as the oxidizer; the working fluid for these engines is made up of nitrogen and the products of propellant combustion. Engines of this type are installed on flying craft operating in the lower layers of the atmosphere (up to 15 to 25 km), in military and civilian jet aircraft, in pilotless aircraft, and in the various systems employed in rocket launching.

Rocket engines are intended for rockets. In terms of propellant, these engines are subdivided into liquid and solid engines [engines operating on liquid and solid propellants, respectively].

Liquid rocket engines, and occasionally solid rocket engines, are used on a large scale for the investigation of the upper layers of the atmosphere, i.e., at altitudes between 50 and 1500 km.

Much progress has been recorded in recent years in the study of outer space by means of rockets with powerful engines capable of overcoming the force of terrestrial gravitation. For example, over the

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past few years tens of satellites have been sent into orbit around the Earth. Cosmic rockets have been sent to the Moon and Venus and have also become artificial satellites of the Sun. And, finally, Major Yuriy Gagarin and Major Gherman Titov, aboard the space vehicles "Vostok" and "Vostok-2" from the Soviet Union, were the first to penetrate outer space, orbit the globe, and return to Earth.

Air-reaction and rocket engines are used on various types of flying craft, but they are also frequently used in combination. For example, in a number of cases rocket engines are mounted on jet aircraft in addition to the air-reaction engines; liquid and solid rocket engines are used on a great scale to assist aircraft on takeoff; and air-reaction engines are sometimes used to accelerate rockets in the atmosphere.

In connection with the widespread application of new types of propellants, we have before us a new field of knowledge — the physics and the chemistry of liquid and solid reaction (rocket) propellants — and this discipline seeks to study the relationship between the chemical composition and the properties of the propellants as they are used in engines, as well as to develop propellant-production methods, i.e., to study all that pertains to the scientific basis for the production and application of reaction propellants.

While the literature (monographs, collections, etc.) on reaction engines in the Soviet Union and abroad is quite extensive, the literature on the chemical composition of propellants for reaction engines is quite limited.

In this connection, the author attempted in his book to generalize the extensive material in the literature on this problem, said data found primarily in journals. This book is a revised and considerably expanded version of the author's monograph "The Chemical Composition

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and Properties of Reaction Propellants" which was published in 1958.

Of course, the book is not free of flaws, but these are due to newness of the problem, and the author will gladly receive any comments from the readers.

Professor Ya.M. Paushkin

INTRODUCTION

The widespread development during the past 10 to 20 years of reaction engineering with its liquid and air-reaction engines was preceded by an extensive period (more than half a century) during which the theoretical foundations for reaction-thrust motion were being worked out.

The theoretical fundamentals of reaction engineering were first presented in works of the outstanding Russian scientist K.E. Tsiolkovskiy (1857-1935), more than 50 years ago. As early as 1898, K.E. Tsiolkovskiy — after extensive work — derived the mathematical theories for the flight of a rocket craft and the functioning of a reaction engine, said theories published by him in 1903. In these works, in addition to discussing the theoretical foundations of reaction-thrust motion, hydrocarbon and liquid-oxygen fuels were proposed for the first time as propellants for reaction engines.

Later on, K.E. Tsiolkovskiy pointed out methods of using reaction engines for flights within the atmosphere, using the oxygen of the air as the oxidizer. This principle is employed today in aircraft with air-reaction engines.

K.E. Tsiolkovskiy was the first to resolve the following problems: he proposed the principles and design for a liquid rocket engine, and he suggested the utilization in rocket engines of liquid oxygen, liquid ozone, and the oxides of nitrogen as oxidizers: he suggested the use of hydrocarbons and hydrogen as the combustible (fuel); he derived the formula for the maximum flight velocity of a rocket at the end of

the active phase and this formula is of great and basic importance; he proposed the principle of employing a pump for the pressurized feed of the propellant into the combustion chamber of an engine, and it was also his idea to use one of the components of the propellant for the purpose of cooling the engine chamber; he laid the basis for the utilization of graphite and high-melting metals for the fabrication of nozzles and engine chambers; he proposed the use of control surfaces situated in the stream of the gases flowing out of the engine nozzle for purposes of rocket-flight control; he laid the groundwork for the various aspects of using rockets in the study of outer space; he presented the idea of using composite and multistage rockets to attain cosmic flight velocities; he developed the theory of using winged reaction-thrust missiles to achieve great flight range in the atmosphere; and it was he who expressed the idea of designing a jet aircraft capable of using the oxygen of the air in its engine.

K.E. Tsiolkovskiy left us with a great scientific legacy: prior to the Great October Socialist Revolution he published some 50 works, and after the Revolution he published more than 150 works.

In the history of the development of rocket engineering, in addition to K.E. Tsiolkovskiy, we will forever find the name F.A. Tsander (1887-1933) — a Russian engineer and a firm believer in the possibility of interplanetary flight — who began his work on problems related to interplanetary flight in 1908.

In his book "Problems of Flight with Reaction-Thrust Craft," published in 1932, F.A. Tsander discussed the results of his investigations. He had worked out solutions to such problems as the use of metals in rocket propellants, the principles involved in thermal calculation and the cooling of rocket-engine chambers, the theory of rocket flight along an elliptical trajectory, the flight of an air-

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craft with a jet engine, the selection of the most efficient propellants for rocket engines, and he was the first in the Soviet Union to design rocket engines operating on oxygen.

Yu.V. Kondratyuk (1900-1941) is another of the pioneers in rocket engineering in the Soviet Union; he began his work in the field of reaction-thrust motion in 1917 and in 1929 published a book entitled "The Conquest of Interplanetary Space." He suggested the use of lithium, boron, and other solid fuels (combustibles) in rocket propellants, and it was he who investigated the dynamics of the takeoff of a winged reaction-thrust craft, and he developed the theory of multistage rockets.

Starting in 1930, the USSR began the development of the first liquid rocket engines. This work was carried out by two groups of engineers and scientists in Moscow and Leningrad.

In the period from 1930 to 1940, quite much was done in this field, particularly if we take into consideration the level of engineering at that time.

For example, in 1930 the small rocket engine ORM-1, developing a thrust of 20 kg, was designed and built; this engine operated on oxides of nitrogen and toluene.

In 1933 an engine was built to operate on liquid oxygen and jellied gasoline. The gasoline was placed directly into the combustion chamber, and the liquid oxygen was supplied from a special tank. This engine was mounted on the "09" rocket and developed a thrust of 52 kg for 15 to 18 seconds. The first Soviet rocket with this engine was launched on 17 August 1933. The rocket had a launch weight of 18 kg and it was 2.4 meters long.

In 1932-1933, under the guidance of F.A. Tsander, the liquid rocket OR-2 engine, operating on liquid oxygen and gasoline, was built;

this engine developed a thrust of between 50 and 100 kg.

The OR-2 engine was tested on the GIRD-X rocket which was launched on 25 November 1933. The rocket weighed 29.3 kg and it was 2.2 m long; the engine developed a thrust of 70 kg for a period of 22 seconds. The rated altitude of the rocket was 5.5 km. The OR-2 engine was also designed to be mounted on a rocket glider.

In 1932, work was begun on the design of a liquid reaction engine with a turbopump assembly and capable of developing from 500 to 5000 kg of thrust.

In 1933, the ORM-52 rocket engine was built; this engine, operating on nitric acid and kerosene, was extremely large for its time.

In 1934, the "07" rocket with a liquid-oxygen and ethyl-alcohol engine was built. The flight tests of this rocket were carried out on 17 November 1934. The engine developed a thrust of 80 to 85 kg for 22 to 27 seconds. The flight range of the rocket was some 4 km.

From 1934 to 1937 work was being done on improving and developing new liquid rockets.

In April of 1935 a liquid-oxygen and ethyl-alcohol rocket was tested; this rocket flew a distance of 5.5 km.

By 1936 the rather large 12/K alcohol and liquid oxygen engine had been developed; this engine was rated for a thrust of 300 kg. It was mounted on the "05" rocket which was 3.2 m long and 0.3 m in diameter; the launching weight of the rocket was 89 kg and the engine developed a thrust of 205 kg. This rocket, together with this engine, was flown on 5 April 1936.

In April of 1937 tens of rockets with alcohol and liquid-oxygen engines were launched to altitudes of 3.5 and 4.5 km in vertical flight.

In 1939 tests were completed on the winged "212" rocket on which an ORM-65 engine was mounted; this engine operated on nitric acid and

kerosene; this engine was capable of developing a thrust of 175 kg. The rocket was equipped with an automatic autonomous control system. The flight range for the rocket amounted to some 50 kilometers.

From 1935 to 1937 the USSR was engaged in the development of yet another rocket, this one weighing some 100 kg, with the launching taking place in 1937. The rocket attained an altitude of approximately 3000 meters.

From 1933 to 1940 twelve types of various stratospheric rockets were designed. In this same period, a rocket engine was designed for aircraft, said engine to operate on kerosene and nitric acid. This engine was capable of developing a thrust of 140 kg, and the engine itself weighed some 100 kg. The engine was mounted on the RP-318 rocket glider which was capable of developing a speed of 200 km/hr. This rocket glider first flew on 28 February 1940.

By 1939-1940 the Soviet Union had produced experimental models of unguided liquid rockets capable of covering a distance of 25 km, and these rockets underwent their flight tests successfully.

From 1918 through 1938-1940 Oberth, Braun, Zenger, et al., in Germany, and Goddard in the USA were in charge of investigations carried out by groups of inventors in the field of reaction engineering. As a result of these efforts, by 1934-1935 a number of small rockets with liquid reaction engines had been built, and these rockets attained altitudes of 2-2.3 km. It was Braun in Germany who was in charge of the serious work in this field, begun in 1938 and completed in 1944 with the development of a long-range rocket (with a flight range of 300 km).

On the eve of the 1941-1945 war the Soviet Union had produced rocket installations using solid-propellant rockets which were known as "Guard rocket launchers" ("Katyush") which played so important a

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role during the years of the Fatherland War.

After the war, the rocket-building industry developed extensively throughout the Soviet Union and as a result the Soviet Army was equipped with the latest rocket weapons.

In August of 1957 the first multistage intercontinental ballistic rocket was tested in the Soviet Union. The rocket tests were carried out successfully and the rockets vindicated completely the calculations that had been carried out and the designs that had been selected.

The construction of an intercontinental rocket made a great contribution to the defensive capabilities of the Soviet Union.

On 4 October 1957, in the USSR, the first successful launching of an artificial satellite of the Earth in the history of mankind was carried out by means of a multistage rocket.

On 3 November 1957, in the Soviet Union, the second artificial satellite of the Earth was launched, and this vehicle was equipped with scientific equipment and there was an experimental animal aboard — a dog. The measurement data produced by the scientific equipment and the behavior of the animal during the motion of the satellite in outer space about the earth were transmitted to Earth by means of radio signals.

On 15 May 1958 the third artificial satellite of the Earth was launched, and this vehicle completed more than 10,000 revolutions about the Earth during the almost 2 years of its existence.

Later on, in September and October of 1959, in the Soviet Union, space rockets were launched to the vicinity of the Moon, flying around the Moon, and transmitting television images of the lunar surface back to Earth.

During 1960-1961, in the Soviet Union, several satellite vehicles and powerful rocket boosters were developed, the latter being used to

carry the former into orbit. The satellite vehicles were tested successfully and methods have now been worked out for the safe return to Earth of experimental animals aboard these space vehicles.

Soviet scientists and engineers made a tremendous contribution to the scientific efforts of the world, and prepared the way for the flight of man into the cosmos, through the successful construction and launching of the artificial satellites of the Earth and the space rockets. This flight of man into outer space took place on 12 April 1961 aboard the Soviet satellite vehicle "Vostok" which was put into orbit by a powerful rocket with six engines developing a total power of 20,000,000 horsepower. The weight of the vehicle, without the last stage of the rocket, amounted to 4750 kg, and the flight lasted 108 minutes.

The second manned flight into outer space, in an orbit around the Earth, was also carried out in the Soviet Union in August of 1961, and this flight lasted 25 hours.

The satellite vehicles "Vostok" and "Vostok-2" were fitted out with a pilot's cockpit and an instrument section which housed a variety of equipment and the reverse-thrust rocket engine ("retro-rocket") of the vehicle. It was possible to carry out observations throughout the entire flight and during deceleration in the atmosphere from the cockpit through observation windows that had been fitted out with heat-resistant glass, since the temperature of the vehicle's surface attains thousands of degrees on re-entry. The vehicle also contained equipment needed for man to exist, as well as flight-control equipment, and such apparatus as was required from the standpoint of scientific observations; in addition, there was a manual control system for the vehicle.

In order to land the vehicle at a designated point, it was fitted

out with reverse-thrust rocket engines and a vehicle-orientation system which made use of the Sun in order to enable the pilot to determine and maintain his required heading with great accuracy as the vehicle turned about the earth; the food and water supply, the air-regeneration system, and the power sources for the electrical systems were designed and calculated to permit a flight of 10 full days.

Thus man, for the first time ever, overcame the force of terrestrial gravitation — he completed a flight into outer space and returned to Earth.

The Soviet Union has achieved much in the construction of jet engines. In the period from 1956 to 1960 improved passenger jet aircraft were built. Various types of Soviet aircraft (with seating capacities ranging from 70 to 180-220 passengers), with powerful turbojet engines, are capable of speeds up to 900-1000 km/hr at an altitude of 10-12 km, with a continuous flight range of 3000-3500 km and more. In 1957, the largest passenger aircraft in the world was built; this is the TU-114 which uses turboprop engines and is intended for nonstop intercontinental flights.

The Soviet Union also has heavy intercontinental supersonic aircraft.

The rapid and intensive development of reaction engineering, starting right after the war, opened a new and multifaceted area of scientific investigation.

Although the design principles behind reaction-thrust engines are considerably simpler than those involved in the case of piston engines, it does not necessarily follow that the engine cycle has correspondingly been simplified. Quite the contrary, the cycle of a reaction engine involves a considerably more complex collection of physical, physicochemical, and chemical phenomena.

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Part One

HYDROCARBON FUELS (PROPELLANTS) FOR AIR-REACTION AND ROCKET ENGINES

Chapter 1

GENERAL DATA ON AIR-REACTION AND LIQUID REACTION ENGINES

1. Characteristics of Individual Types of Air-Reaction Engines

The following types of air-reaction engines [1-6] have found application among jet aircraft:

1) turbojet engines (TRD);

2) turboprop engines (TVD);

3) flow-through air-reaction engines [ramjets] (PVRD);

4) pulsating air-reaction engines [pulsejets] (PuVRD); this type of engine was used primarily during the first stages of the development of reaction engineering;

5) bypass turbojet engines;

6) atomic air-reaction engines (employing the atomic energy produced by nuclear reactions).

In turbojet engines (Fig. 1) the approaching flow of air is compressed by means of a compressor and is introduced into the combustion chamber to which fuel is supplied. At supersonic flight velocities, substantial air compression comes about through the deceleration of the flow. The fuel-burning process, depending on the design of the engine, may take place in several combustion chambers (which is the case with cannular engines) or in a single annular chamber. As a result of the burning of the fuel in the primary combustion zone, given an excess-air ratio close to unity, temperatures of 1900 to 2200° are developed. In order to reduce the temperature of the products of combustion, excess air is supplied to the secondary zone of the combustion

chamber, with this air flushing the chamber and expanding the products of combustion. As a result, the temperature of the products of combustion together with the air drops to 750-850° at the end of the chamber. Subsequently, the products of combustion at a temperature of 650-800° impinge on the buckets of the gas turbine causing the latter to rotate. The turbine is situated on a single shaft with the compressor. The turbine shaft rotates at 8000-16,000 rpm.

In their passage through the gas turbine the gases accomplish work and then subsequently enter the propulsion nozzle of the engine from which they are discharged, at a temperature of 500-600°, producing reaction thrust.

In turboprop engines (Fig. 2) a propeller is mounted on the shaft of the gas turbine and compressor. Thrust is produced by the rotation of the propeller and partially by the gases being discharged through the nozzle of the engine. The reaction force is not great and amounts to 15-20% of the total thrust of the engine which can attain 250-300 kg. Engines of this type are characterized by great operating economy. The fuel flow rate at maximum power is less than 0.2 kg/hp·hr.

In ramjet engines (Fig. 3), given great flight velocities, the air is forced into the combustion chamber of the engine by the approaching stream and is compressed on deceleration. Fuel is injected into the combustion chamber, vaporized, mixed with air, ignited, and burned. The heated products of combustion that are formed as a result move out through an open section in the engine at the opposite end — the nozzle — thus producing reaction thrust. In order for the efficiency of the engine to be sufficiently high, the incoming air must be compressed at least by a factor of 2 to 3, and this can be accomplished at a flight velocity considerably in excess of the speed of sound, i.e., 1200 km/hr and higher. Thus ramjet engines are intended for

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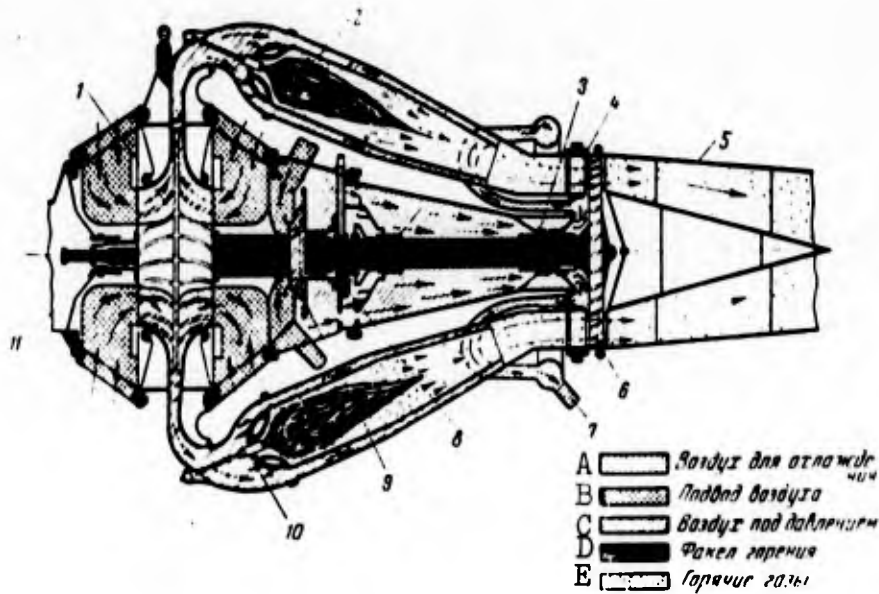
Fig. 1. Turbocompressor air-reaction engine. 1)
Centrifugal compressor with admission of air to
both sides of the compressor; 2) ten direct-flow
combustion chambers; 3) rear bearing; 4) nozzle
rim; 5) propulsion nozzle; 6) single-stage turbine;
7) outlet for cooling air; 8) central bearing; 9)
cooling fan for turbine and rear bearing; 10) ten
open-type injectors; 11) forward bearing; A) cool-
ing air; B) air supply; C) air under pressure; D)
combustion flame; E) hot gases.
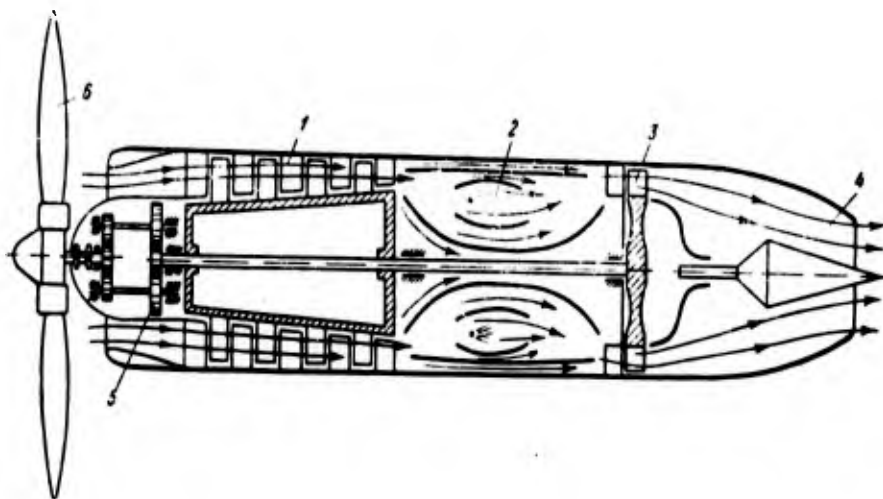
Fig. 2. Schematic diagram of a turboprop engine.
1) Compressor; 2) combustion chamber; 3) gas tur-
bine; 4) nozzle; 5) reduction gear; 6) propeller.

supersonic flight. A diagram of a ramjet engine is presented in Fig. 4.

In pulsejets (Fig. 5) the approaching air passes through an open-
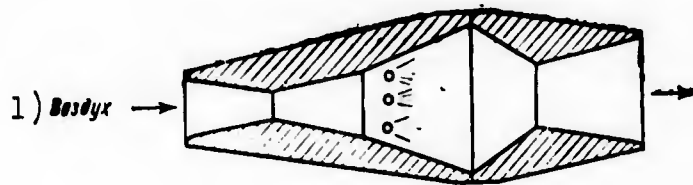
Fig. 3. Schematic diagram of a supersonic direct-flow air-reaction engine [ramjet]. 1) Air.
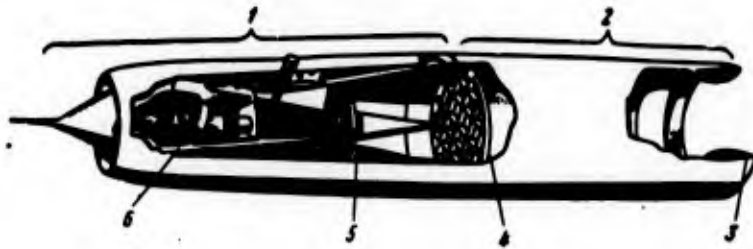
Fig. 4. Supersonic direct-flow air-reaction engine [supersonic ramjet]. 1) Diffuser; 2) combustion chamber; 3) exit (exhaust) nozzle; 4) flame holder; 5) fuel injectors; 6) fuel pump.
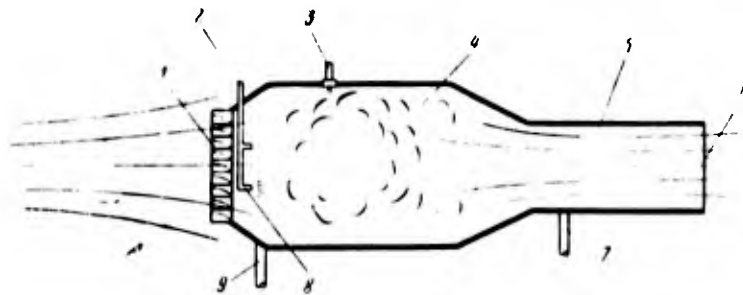
Fig. 5. Schematic diagram of pulsating air-reaction engine [pulsejet]. 1) Valve box assembly; 2) fuel manifold; 3) spark plug; 4) combustion chamber; 5) tailpipe; 6) outlet; 7) rear support; 8) fuel injectors; 9) forward support.

ing in the forward section of the engine and moves into the combustion chamber, in front of which the air stream is decelerated.

The air is mixed with the vaporized fuel (combustible), after which the fuel mixture is ignited by an electric spark plug. The pressure within the combustion chamber is raised, as a result of which the inlet valves at the head of the engine are closed, and the products of combustion escape at great velocity through the tailpipe — the nozzle,

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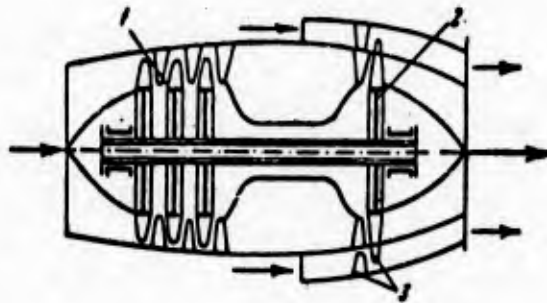
Fig. 6. Schematic diagram of bypass [two-contour] turbojet engine. 1) Compressor; 2) turbine; 3) compressor for outer duct.

thus producing a reaction force. As the gases are propelled out of the combustion chamber of the engine, the pressure within the engine is therefore evacuated and the approaching air stream opens the valves, again filling the engine with air and vaporized fuel, after which the cycle is repeated. The pulsating engine completes from 50 to 150 cycles each second. The filling of the engine with air and the fuel mixture, the burning process, and the discharge of the gases involves no more than 6 to 20 milliseconds. The engine cycle is started by forcing compressed air through the valve box.

Bypass turbojet engines (Fig. 6) differ from other turbojet engines in that this engine has an additional external duct into which air is forced by means of an annular compressor in which the air has been compressed and from which it flows out through an annular nozzle, thus producing additional thrust. The cycle in the inner duct is similar to the cycle in a turboprop engine.

However, the turbine of the basic engine duct produces an excess of power which is expended on actuating the compressor of the external duct. The compressor of the external duct is essentially a high-speed impeller enclosed in an annular tunnel through which an additional quantity of air passes.

Bypass engines exhibit lower specific fuel consumption than do

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turbojet engines; however, at supersonic speeds this advantage is lost if an additional quantity of fuel is not burned in the external duct.

Atomic air-reaction engines use the energy produced by the nuclear reactions of an atomic fuel [6a]. This energy goes to heat the air (in its passage through the engine) which serves as the working fluid and produces thrust.

Several companies have been working in the USA since 1954 on the production of atomic air-reaction engines [6].

The basic obstacle preventing the utilization of nuclear energy for aircraft engines is the tremendous weight required for the shielding which is needed to protect the crew and passengers against the harmful radiation emitted by the reactor. This weight is estimated to be of the order of 100 tons. The basic problem therefore is to reduce this weight to 40 to 50 tons, which weight would correspond to the weight of the fuel supply for a large aircraft.

There is an atomic aircraft on the drawing boards which will be capable of carrying 180 passengers at a velocity of 1600 km/hr for virtually unlimited distances. The first version of this aircraft will cost 12-15 times more than a contemporary large jet transport [6].

Plans are underway for an atomic jet aircraft weighing about 100 tons whose power plant will be capable of producing 30,000 horsepower.

In the construction of atomic aircraft we must resolve complex problems associated with the techniques of heat transfer and the development of various types of controlled reactors capable of functioning at rather high temperatures, i.e., at least 800 to 1000°.

Apparently these difficulties are gradually being overcome. For example, it was reported in 1956 that ground tests of a nuclear turbojet aircraft engine were being started in the USA. This engine was operated for the first time in January of 1956 on thermal energy obtained

from an experimental nuclear reactor.

Plates (flats) of stainless-steel clad UO_2 were used as the fuel elements for this reactor.

The temperature of the fuel attains 1000°, and conventional water is used as the moderator; the coolant, air in this case, is supplied directly into the gas turbine [7].

In all probability, it would be easier during this first stage of the project to design a radio-controlled pilotless atomic aircraft which would not require the somewhat complex shielding against the radioactive emissions of the reactor.

2. Conversion of the Thermal Energy of the Fuel (Propellant) into Work in Air-Reaction Engines

In air-reaction energy, the thermal engine of the fuel is converted into the kinetic energy of the products of combustion. The fuel is supplied to the engine from tanks and burns because of the oxygen in the air which is admitted into the engine. The mixture of the heated products of combustion and the air is discharged through the engine nozzle at a great velocity thus producing reaction thrust.

For each part of fuel weight, some 14 to 16 parts of air enter the combustion chamber; this air is necessary for complete combustion. However, a three- or five-fold excess of air (50-80 parts of air, by weight, for each part of fuel, by weight) is generally supplied to the engine, and a part of this excess (about 20%) is employed for the combustion of the fuel, with the remaining part (about 80%) used for the cooling of the engine and the dilution of the products of combustion in order to reduce the temperature of the latter before they reach the turbine buckets.

Let us examine briefly the process involved in the conversion of the thermal energy of the fuel into mechanical work in air-reaction

engines [2-4].

The exhaust velocity of the products of combustion and that of
the excess air, attained as a result of the combustion of the fuel in
the engine, is associated with the heating value of the fuel in accord-
ance with the law governing the conversion of the potential thermal
energy of the fuel into kinetic energy:

$$\frac{G_{\text{a}}(u^2-v^2)}{2g} = \frac{1}{A}\cdot\eta_t\cdot G_{\text{T}}\cdot Q_{\text{H}},$$

where G_v is the per-second air flow rate passing through the engine
(kg/sec); G_t is the per-second fuel flow rate through the engine
(kg/sec); Q_H is the specific heating value of the fuel (kcal/kg); A =
= 1/427; $\underline{u}$ is the exhaust velocity of the products of combustion
(m/sec); $\underline{v}$ is the velocity of the approaching air stream, in m/sec
(it is equal to the flight velocity); η_t is the thermal efficiency.

The kinetic energy of the fuel mass in the left-hand part of the
equation can be neglected, since it is small in comparison with the
mass of the air passing through the engine.

The thermal efficiency characterizes the fraction of the thermal
energy of the fuel that is converted into mechanical work, and this
can be given, in approximate terms, by the following expression:

$$\eta \sim \frac{C_1 T_{\text{rop}} - C_2 T_{\text{conл}}}{C_1 T_{\text{rop}} - C_3 T},$$

where T_{gor} is the burning temperature; T_{sopl} is the temperature of the
gases being discharged through the engine nozzle; T is the temperature
of the approaching air stream; $C_{1,2,3}$ are heat capacities.

The per-second flow rates of air and fuel are associated by the
following relationship:

$$G_{\text{a}} = \alpha L_0 \cdot G_{\text{т}},$$

where α is the excess-air ratio (generally, 3-5); L_0 is the quantity
of air (kg) needed to burn 1 kg of fuel (14-16 kg).

With respect to 1 kg of air, the kinetic energy of the air is associated with the thermal energy of the fuel by the following relationship:

$$\frac{u^2 - v^2}{2g} = \frac{1}{A}\,\eta_t\,\frac{Q}{\alpha L_0}. \tag{1}$$

The exhaust velocity of the air and the products of combustion is found by means of Eq. (1)

$$u = \sqrt{2g \cdot \frac{1}{A}\,\eta_t\,\frac{Q}{\alpha L_0} + v^2}\ \ \text{m/sec.} \tag{2}$$

But since

$$\frac{Q}{\alpha L_q} = C_p(T_{cr} - T)$$

(T_{sg} is the air temperature attained as a result of the combustion of the fuel; T is the temperature of the air in front of the combustion chamber; C_p is the heat capacity of 1 kg of air), we can write the expression for the exhaust velocity in the following form:

$$u = \sqrt{2g\,\frac{1}{A}\,\eta_t C_p\,(T_{cr} - T) + v^2}\ \ \text{m/sec.} \tag{3}$$

The thermal efficiency is determined, in turn, by the following expression:

$$\eta_t = 1 - \left(\frac{p_i}{p_0}\right)^{\frac{k-1}{k}},$$

where p is the air pressure in front of the nozzle; p_0 is the pressure at the nozzle outlet; $k = C_p/C_v$.

In addition to Eqs. (2) and (3), the theoretical exhaust velocity for the products of combustion from a VRD [air-reaction engine] can be given by the following equation:

$$u = \sqrt{2g\,\frac{k}{k-1}\,RT\left[1 - \left(\frac{p_0}{p}\right)^{\frac{k-1}{k}}\right]}\ \ \text{m/sec,} \tag{4}$$

where p is the pressure of the products of combustion in front of the nozzle; p_0 is the pressure at the nozzle outlet; T is the temperature

of the air and of the products of combustion in front of the nozzle.

In a turbojet engine the temperature of the air and of the products of combustion in front of the nozzle is lower than in the case of a direct-flow engine [ramjet] because of the work expended on the turbine.

The specific thrust can be determined in terms of the exhaust velocity of the products of combustion, i.e., we can determine the thrust referred to 1 kg of air which is the working fluid.

The total thrust of a reaction engine is found to be a function of the per-second flow rate of the working fluid in accordance with the familiar relationship between thrust and exhaust velocity:

$$R = \frac{G}{g} \cdot u,$$

where G is the per-second flow rate of the working fluid; g is the force of gravitational acceleration, equal to 9.81 m/sec^2.

But for a VRD in flight, the exhaust velocity u must be reduced to the velocity of the approaching air stream in order to obtain the thrust developed as a result of the fuel combustion:

$$R = \frac{G_b}{g}(u - v) + \frac{G_r}{g} \cdot u, \qquad (5)$$

where G_v and G_t are the per-second flow rates of air and fuel; v is the axial velocity of the working fluid (air) entering the engine, said velocity equal to the velocity of flight.

Since the flow rate of the fuel in an air-reaction engine is less by a factor of 60 to 80 than the flow rate of the air passing through the engine cross section, the second term in Eq. (5) is frequently neglected. In this case, the error in the determination of thrust does not exceed 1.5-2%.

In this case, the specific thrust of an air-reaction engine is

$$R_{ud} = (u - v)/g \text{ kg of thrust} \cdot \text{sec/kg of air}$$

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$$R_{y\text{д}} = \frac{1}{g}\left\{\sqrt{2g\frac{k}{k-1}RT\left[1-\left(\frac{p_0}{p}\right)^{\frac{k-1}{k}}\right]} - v\right\}.$$

For a direct-flow [ramjet] engine

$$R_{y\text{д}} = \frac{1}{g}\left\{\sqrt{2g\,427\eta_i\frac{Q}{aL_0} + v^2} - v\right\}.$$

For the operating characteristics of air-reaction engines we use the concept of specific fuel consumption, in kg per 1 hour, for the development of 1 kg of thrust:

$C_{ud} = (G_t \cdot 3600 \cdot \text{hourly fuel flow rate})/\text{thrust} = g_t(3600/R_1)$,

where R_1 is the specific impulse (kg of thrust·sec/kg of fuel), i.e., the ratio of the thrust force to the per-second fuel flow rate. R_1 is associated with R_{ud} — the specific thrust referred to 1 kg of air in the following manner:

$$R_i = \frac{R_{y\text{д}}}{g_\text{т}},$$

where g_t is the weight ratio of the fuel to the air entering the engine.

In connection with the above, the specific fuel consumption can be presented in the following form:

$$C_{y\text{д}} = \frac{3600 \cdot g_\text{т}}{\frac{1}{g}\left\{\sqrt{2g\,427\eta_i\eta_g\frac{Q}{aL_0} + v^2} - v\right\}} \quad \text{kg of fuel/kg of thrust·hr}$$

or as follows:

$$C_{y\text{д}} = \frac{3600 \cdot g_\text{т}}{\frac{1}{g}\left\{\sqrt{2g\frac{k}{k-1}RT\left[1-\left(\frac{p_0}{p}\right)^{\frac{k-1}{k}}\right]} - v\right\}}.$$

On the other hand, the specific fuel consumption can be determined by the familiar relationship

$$C_{y\text{д}} = A \cdot \frac{3600 \cdot v}{\eta_0 Q}$$

where η_0 is the total efficiency of the flying craft, i.e.,

$$\eta_0 = A\,\frac{\text{Energy of reaction craft motion}}{\text{Thermal energy obtained on combustion of fuel}}$$

or

$$\eta_0 = A \frac{R \cdot v}{G_{\tau} \cdot Q}.$$

The total efficiency is the product of the following three coefficients

$$\eta_0 = \eta_t \cdot \eta_g \cdot \eta_n,$$

where η_t is the thermal efficiency which characterizes the engine as a heat machine; η_g is the relative coefficient which indicates the extent to which the actual exhaust velocity differs from the theoretical velocity; η_p is the flight efficiency which determines the ratio of the energy of reaction-craft motion to the difference between the kinetic energies of the air leaving and entering the engine, plus the kinetic energy expended by the fuel.

The flight coefficient is determined, in final form, by the following ratio:

$$\eta_n = \frac{2\frac{v}{u}}{1 + \frac{v}{u}} = \frac{2v}{u + v}.$$

The flight efficiency is a function of the ratio v/u; at v = = const, η_p diminishes with an increase in $\underline{u}$. For example:

$\frac{v}{u}$	η_n
1	1
0,5	0,65
0,2	0,30

Therefore, in the expression for the specific consumption:

$$C_{y\pi} = A \cdot \frac{3600 \cdot v}{\eta_0 \cdot Q}$$

the quantity C_{ud} is not uniquely defined by the heating value, since $\underline{u}$ changes with a change in the latter, and η_0 also changes, and this can be presented in the following fashion:

$$C_{y\pi} = A \cdot \frac{3600 \cdot 2\,(u + v)}{\eta_g \cdot \eta_t \cdot Q}.$$

The higher the heating value of the fuel, the lower the fuel consumption for the development of the given thrust, and in the final analysis this increases both the duration and range of aircraft flight.

Flight range is also determined by the fuel reserve in the tanks, and this reserve is associated with the density of the fuel. The higher the fuel density, the greater quantities of fuel can be stored in the tanks of the aircraft. However, in this case the starting (takeoff) weight of the aircraft increases, and this in turn has an unfavorable effect on range.

We have the following familiar relationship for the determination of the flight range of a jet aircraft [5]:

$$S = \frac{3.6\,av}{C_{y\text{д}}} \cdot \ln \frac{U_{\text{сам}} + w\rho}{C_{\text{сам}}},$$

where $\underline{v}$ is the flight velocity; C_{ud} is the specific fuel consumption; G_{sam} is the weight of the aircraft, without fuel; $\underline{w}$ is the volume of all tanks; ρ is the density of the fuel; $G_{sam} + w\rho$ is the takeoff weight of the aircraft, without counting a possible bomb load); $\underline{a}$ is a coefficient.

Denoting the ratio w/G_{sam} by the letter γ, we can write

$$S = \frac{3.6\,av}{C_{y\text{д}}} \cdot \ln (1 + \gamma \cdot \rho),$$

where γ is the index for the particular aircraft design, i.e., the characteristic quantity for an aircraft of a certain design.

Replacing C_{ud} by its value

$$C_{y\text{д}} = A \cdot \frac{3600 \cdot v}{\eta_\theta \cdot Q},$$

we will obtain the equation of range in the following form:

$$S = a \cdot k \cdot \eta_0 \cdot Q \ln (1 + \gamma \cdot \rho),$$

where $\underline{k}$ and $\underline{a}$ are coefficients that are functions of flight velocity.

With the range formulas it is possible, in approximate terms, to

estimate the effect of the various factors on flight range.

Flight range is a function of specific fuel consumption or the heating value, density, and reserve of the fuel on-board the aircraft.

In general, flight range under approximately comparable conditions increases with an increase in the total reserve of thermal energy aboard the aircraft, said energy concentrated in the fuel.

3. Area of Application of Air-Reaction Engines [8]

Air-reaction engines are used as power plants on interceptors, bombers, aircraft-missiles, and similar types of military aircraft, as well as on civilian transport aircraft.

The development of military jet aircraft is proceeding so rapidly that it is the characteristic of the contemporary state of aircraft construction that today's aircraft may be obsolete tomorrow.

The obvious characteristics of engines and aircraft are the thrust and velocity developed by the aircraft, ceiling, and range. The power of the air-reaction engines installed on military aircraft attains 12,000-18,000 horsepower and corresponds to a thrust of 4000-10,000 kg. A characteristic velocity of contemporary interceptors is a velocity that exceeds the speed of sound several times, and the operating ceiling is of the order of 24,000 meters. There are aircraft using ramjet engines which can attain even higher flight velocities.

The range of long-range jet bombers varies from 12,000 to 20,000 km. It was reported in 1960 that Soviet interceptors are capable of reaching a ceiling of 28 km [8], and that they are capable of attaining speeds several times in excess of the speed of sound. In 1961, the pilot Fedorov attained a record velocity of 2730 km/hr with a "Ye-166" aircraft.

Until recently, bombers could not exceed the speed of sound. In 1961, supersonic bombers were quite common. For example, the "B-70"

bomber being built in the USA is designed to attain a speed of 3200 km/hr at an altitude of 21 km.

The Soviet Union has supersonic intercontinental bombers armed with rockets [8].

At an air show in 1961, the USSR demonstrated powerful supersonic delta-wing jet bombers, high-speed rocket-carrying aircraft, and heavy naval rocket-carrying aircraft capable of damaging naval and ground targets at great distances with their rockets (Figs. 7 and 8).

A characteristic developmental trend is the ever increasing utilization of turbojet engines in civil aviation. For example, between 1951 and 1953 the British jet transport "Comet-1" completed a number of extensive flights at a velocity of 760 km/hr and a flight range of about 5000 km, with a fuel supply of 22 tons. An improved version of this transport aircraft, the "Comet-4," has just recently been released in Great Britain. The "Caravelle" and the "Lockheed-188" jet aircraft are in use on a number of international airlines. In addition, the "Boeing-707" transport passenger aircraft, designed for 80 to 130 passengers, is being used. This aircraft has four jet engines capable of propelling the aircraft at a speed of 850 to 950 km/hr. Over a distance of 3750 km, an average speed of 947 km/hr was maintained.

The Soviet "TU-104" aircraft is an improved high-capacity passenger jet aircraft. The "TU-104" aircraft (Fig. 9) carries two engines and its maximum velocity is 1000 km/hr; its cruising speed is 800 to 900 km/hr. The aircraft is designed to carry 50 to 80 passengers. The cruising altitude is 10 to 12 km. The "TU-104" covers the distance between Moscow and Omsk (more than 2200 km as the crow flies) in 3 hours; the Moscow-Tbilisi flight takes some 2 hours and 45 minutes; the flight between Moscow and Khabarovsk involves some 10 hours, with one landing en route; the Prague-Moscow-Omsk-Irkutsk-Peking (about 10,000 km) takes

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some 12 hours during which the "TU-104" must make three landings.

In 1957, the Soviet Air Force was strengthened by a series of jet aircraft designed by A.N. Tupolev. For example, the new aircraft "TU-104A" has two turbojet engines which are capable of producing speeds of up to 950-1000 km/hr; the cruising speed of this aircraft is 800 km/hr, its range is 3000 km, and it is designed to carry 70 passengers. An improved version of this aircraft, the "TU-104B," has been released. A new jet aircraft, the "TU-124," with turbofan engines, has recently been released. This is a medium-range aircraft and it can land at comparatively small airfields, since it requires a comparatively short landing and takeoff run; its flight velocity is of the order of 1000 km/hr, and its cruising speed is around 900 km/hr. This aircraft has room for 44 passengers.

Turboprop engines are used for transport aircraft; these aircraft are characterized by their comparatively low flight velocities — to 650-700-750 km/hr and a ceiling of 10-11 km.

The Soviet aircraft industry has produced a series of new passenger aircraft which use turboprop engines.

In 1957, the "TU-114" high-speed passenger aircraft appeared. This aircraft is a free-carrying monoplane with sweptback wings and an empennage, as well as four turboprop engines of great power. This aircraft is designed to transport passengers, cargo, mail, and other loads through the airlanes of the Soviet Union as well as on international routes (Fig. 10).

The quiet flight of the "TU-114" at great altitudes, the excellent heat and sound insulation, comfortable seats, the existence of cabin pressurization systems by means of which it is possible to maintain constant pressure, humidity, and air temperature must ensure conditions during the 10-12-hour uninterrupted flight over a distance of

up to 9000 km, i.e., from Moscow to such distant points as Vladivostok,
Peking, Tokyo, Delhi, Rangoon, etc., under which the passengers will
not become overtired. At the present time, the "TU-114" aircraft, in
terms of passenger and cargo capacity, is the largest passenger air-
craft in the world. The "NK-12M" turboprop engines mounted on this air-
craft exceed by a factor of almost two, in terms of power, all exist-
ing turboprop engines mounted on foreign aircraft. The "TU-114" air-
craft is the fastest passenger aircraft using turboprop engines. In
its conventional version, the aircraft is capable of carrying 170 pas-
sengers; in long-range intercontinental flights, the aircraft can
carry 120 passengers, whereas short flights involving some 1500 to
1800 km, as for example from Moscow to Sochi, the aircraft can carry
220 passengers.

Fig. 7. Soviet supersonic heavy aircraft.

The "TU-114" is a rebuilt bomber which had a range of 17,000 km.
The "IL-18" and the "AN-10," Soviet multiseat turboprop aircraft are
also being used successfully.

In 1961, the Soviet Union released two new helicopters using tur-

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Fig. 8. Soviet supersonic aircraft.
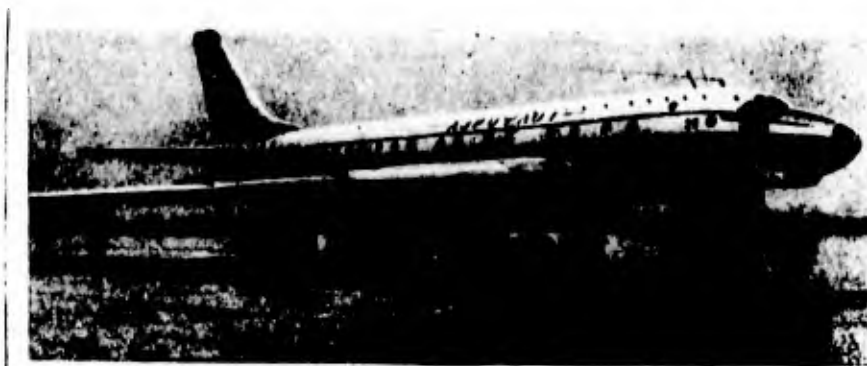
Fig. 9. The "TU-104," a Soviet passenger-carrying
jet aircraft.
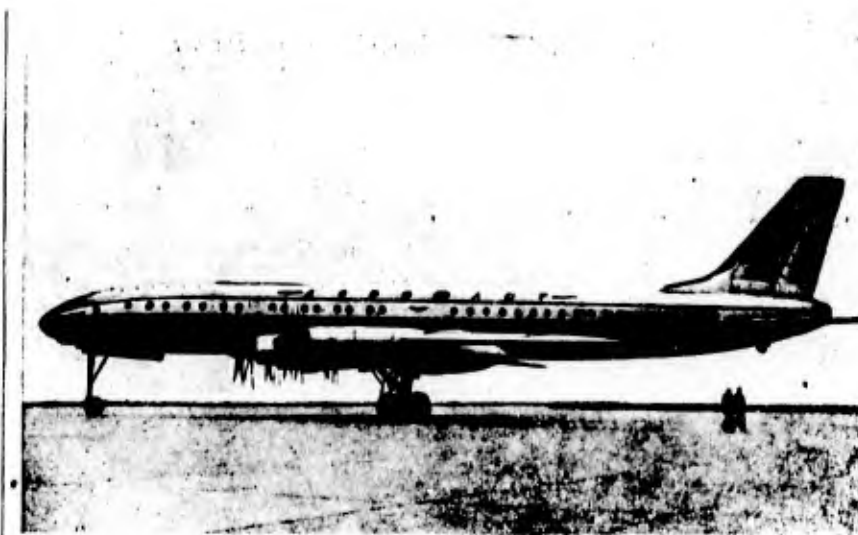
Fig. 10. The "TU-114," a Soviet turboprop passen-
ger aircraft.

boprop engines — the "V-2" and the "V-8" — which can carry 6-8 and 20-26 passengers, respectively.

4. Liquid Reaction Engines

At the present time, liquid reaction engines are used as the power plant for rockets, as units to facilitate aircraft takeoffs, and comparatively less frequently as engines for supersonic aircraft, primarily for interceptor-fighter aircraft. The theoretical principles governing liquid reaction engines and the problems involved in their operation are covered in sufficient detail in the literature [9-15].
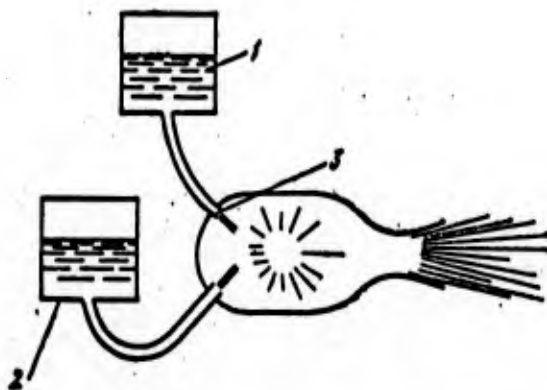
Fig. 11. Schematic diagram of the operation of a liquid reaction engine. 1) Oxidizer tank; 2) fuel (combustible) tank; 3) combustion chamber.

Liquid reaction engines (ZhRD) [liquid rocket engines] consist of a combustion chamber, tanks from which the propellant is supplied, and systems of propellant feed and control.

The majority of ZhRD operate on propellants consisting of two components: a combustible and an oxidizer, which are contained in two individual tanks. In this case, the oxidizer and the combustible enter from tanks into the combustion chamber where they are vaporized, mixed, and burned; the products of combustion are discharged through the engine nozzle, thus producing reaction thrust. Figure 11 shows a schematic diagram of the operation of a ZhRD.
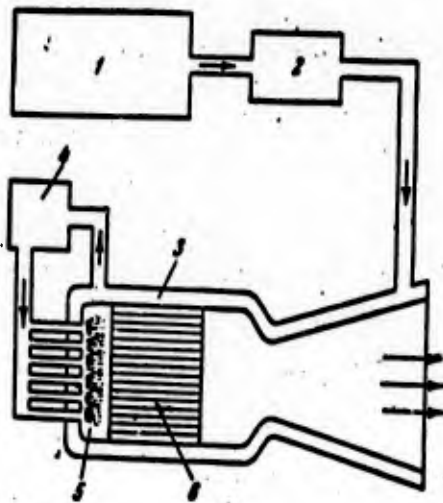
Fig. 12. Schematic diagram of
an atomic liquid reaction en-
gine. 1) Tank with working
fluid; 2) pump assembly; 3)
coolant jacket; 4) control
unit; 5) injectors; 6) atomic
fuel (combustible).

Monopropellant ZhRD are used very much less frequently. A mono-
propellant is stored in a single tank from which it is fed directly to
the engine where it is burned. Therefore, a propellant of this type is
composed both of the oxidizer and combustible elements required for
combustion.

We anticipate, in the future, the appearance of nuclear liquid-
propellant reaction [rocket] engines. The source of the thermal energy
in such an engine would be a nuclear fuel. It will deliver heat to the
working fluid which will heat up to high temperatures and will produce
thrust as it is discharged through the nozzle of the engine. In this
case, the working fluid which will simultaneously be used to cool the
nuclear reactor will be ammonia, water, or similar substances. An op-
erating diagram of an atomic ZhRD is shown in Fig. 12.

Various methods may be employed to supply a liquid propellant to
the engine:

a) by means of compressed gas in tanks, this propellant feed
method is referred to as the pressurized-propellant feed system (Fig. 13);

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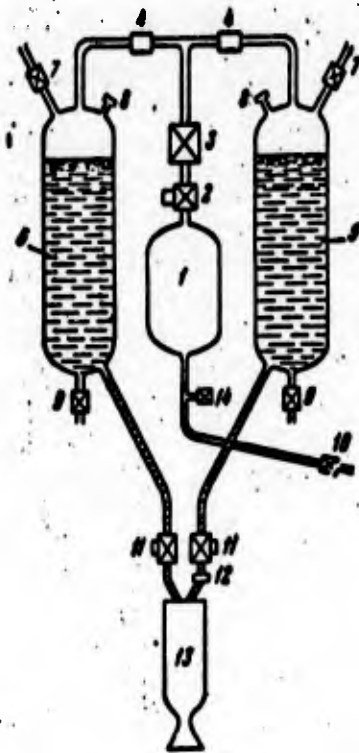
Fig. 13. Diagram of liquid reaction en-
gine with a pressurized-propellant feed
system. 1) High-pressure air tank; 2)
high-pressure air valve (with remote
control); 3) pressure regulator; 4) con-
trol valves; 5) oxidizer tank; 6) pro-
pellant tank; 7) tank vent valves; 8)
filler connections; 9) tank drain valves;
10) pressurizing-gas (compressed air)
feed valve; 11) propellant-feed valve
(with remote control); 12) check valve;
13) combustion chamber; 14) air valve.
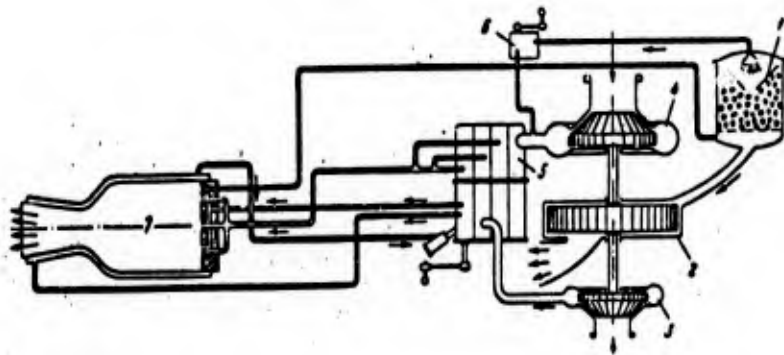
Fig. 14. Diagram of liquid reaction engine with
turbopump feed assembly. 1) Gas generator; 2) tur-
bine; 3) combustible pump; 4) oxidizer pump; 5)
choke assembly; 6) gas-generator valve; 7) reac-
tion engine.

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b) under gas pressure produced through the burning of a solid-propellant grain or other substances at the instant of engine start and operation;

c) by means of turbopump assemblies which pump the propellant from the tanks into the engine; the turbopumps are set into action by means of a gas turbine that operates on a special fuel (Fig. 14); this method is used in rather large rockets.

The propellant-burning process in a ZhRD is carried out at high temperatures (2700-3000°). Therefore, in engines operating for comparatively long periods of time (tens of seconds), the engine walls are cooled by components of the propellant — the oxidizer or the combustible — by means of a jacket or by directing the propellant against the walls. Engines that are in operation for short periods of time (operating for fractions of a second or an entire second) are not cooled at all or are cooled by directing the propellant against the walls.

5. Conversion of the Propellant's Thermal Energy into Work in Liquid Reaction Engines [10, 16, 17]

The thermal energy of the propellant in liquid reaction engines is converted into the kinetic energy of the products of combustion, and this energy is converted into mechanical work in the form of the thrust developed by the engine.

In accordance with the law of the conservation of momentum, the impulse of a body is equal to the products of the force which produces this impulse and the time during which this force is exerted:

$$mv_2 - mv_1 = R \cdot dt,$$

where R is the force acting on a body having mass m; dt is the time during which this force is exerted; $mv_2 - mv_1$ is the impulse of this body during the time dt.

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During the operation of a rocket engine, a burning process takes place within the combustion chamber of the engine, and as a result gases are produced, which are discharged through the nozzle of the chamber at a velocity $\underline{u}$.

With the outflow of the gaseous products of combustion at velocity $\underline{u}$ and having mass $\underline{m}$, some momentum is imparted to the reaction system (the rocket). In accordance with the law of the conservation of momentum, we may write:

$$(m_2 - dm)\, dv = -\, udm; \quad m_2 \cdot dv - dm \cdot dv = -\, udm,$$

where dv is the velocity increment of the reaction system; dm is the mass outflow during the time dt.

Since the value of dm·dv can be neglected,

$$m_2 \cdot dv = -\, u \cdot dm.$$

It follows from the law of the conservation of momentum that the velocity which the reaction device has attained is a result of the action of a certain force during time dt on the reaction engine:

$$Rdt = m_2 dv = -\, udm.$$

Hence the reaction force, or thrust, can be presented in the following form:

$$R = -\frac{dm}{dt} \cdot u$$

or during a period of time equal to 1 second:

$$R = -\, m \cdot u = \frac{G}{g}\, u.$$

Thus the reaction force, or thrust, of a rocket engine can be defined as the product of the mass of the per-second flow rate of the outflowing products of combustion (which is equivalent to the mass of the propellant consumed) by the exhaust velocity of the products of combustion.

The most frequent propellant characteristic that we employ is spe-

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cific thrust, i.e., the thrust referred to 1 kg of propellant mixture:

$$R_{ud} = u/g.$$

The exhaust velocity of the products of combustion from a ZhRD can be found from the conditions of the conversion of the thermal energy of the propellant into the kinetic energy of the products of propellant combustion in accordance with the following equation:

$$\frac{mu^2}{2} = \frac{Gu^2}{2g} = \eta_t \cdot H \cdot E \cdot G,$$

where η_t is the efficiency of the process; E is the mechanical equivalent of heat; $\underline{u}$ is the exhaust velocity; $\underline{m}$ and G are, respectively, the mass and weight of the products of combustion (propellant); H is the heating value of 1 kg of propellant mixture (the mixture of the oxidizer with the combustible). The theoretical exhaust velocity may be presented in the following form:

$$u = \sqrt{2g\,427\eta_t \cdot H}\, \text{m/sec.} \tag{1}$$

After the rearrangement of the constants, this expression takes the following form:

$$u = 91{,}53\,\sqrt{\eta_t \cdot H}\, \text{m/sec};$$
$$R_{уд} = 9{,}33\,\sqrt{\eta_t \cdot H}\, \text{sec}, \tag{2}$$

where η_t is the thermal efficiency which represents the fraction of the thermal energy of the propellant that is converted into mechanical work:

$$\eta_t = \frac{i_1 - i_2}{i_2 - i_0} \sim \frac{C_1 T_1 - C_2 T_2}{C_1 T_1},$$

where i_1 is the heat content (enthalpy) of the product of combustion in the combustion chamber in front of the nozzle; i_2 is the heat content of the products of combustion after the outflow through the nozzle (at the nozzle outlet); i_0 is the heat content (enthalpy) of the propellant; $C_{1,2}$ and $T_{1,2}$ are the corresponding heat capacities and temperatures.

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It follows from the expression presented above that η_t is always other than unity, since the actual temperature of the gases flowing out of the engine nozzle is never equal to the temperature of the ambient medium.

On the other hand, we know from thermodynamics that the thermal efficiency is a function of the ratio of the pressure P_0 at the outlet of the engine nozzle to the pressure P in the combustion chamber, said ratio raised to some power:

$$\eta_t = 1 - \left(\frac{P_0}{P}\right)^{\frac{k-1}{k}},$$

where k is the adiabatic exponent, i.e., the ratio of C_p to C_v; the pressure P_0 at the surface of the ground is close to atmospheric pressure; P_0 diminishes at great altitudes, but not by as much as to become equal to the pressure of the ambient medium as the gases move out from an actual nozzle.* At great altitudes, as a result of the drop in P_0, thermal efficiency increases by 15-20%.

The adiabatic exponent is a function of the composition of the products of combustion, as a result of which η_t diminishes in the case of a transition from biatomic to monatomic products of combustion (Table 1).

It should be pointed out that in addition to the unavoidable losses determined by the thermal efficiency, there exist other forms of losses that are associated with incomplete combustion, heat losses, and expenditures of energy on propellant feed. These losses are determined by the effective efficiency and are examined in detail in special courses dealing with engines.

From Eq. (1) we can derive the following expressions for the exhaust velocities of the gaseous products of combustion from a de Laval nozzle:

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TABLE 1

Change in Thermal Efficiency as a Function of the
Nature of the Products of Combustion and of the
Pressure in the Chamber

1 Газы		k	$\dfrac{k-1}{k}$	2 Термический к. п. д. при давлении, am					
3 Число атомов в молекуле	4 Пример			20	25	40	50	70	100
1	H, N	1,667	0,4	0,608	0,7240	0,7714	0,7900	0,8173	0,8415
2	CO, N₂	1,286	0,222	0,451	0,5122	0,5631	0,5824	0,6123	0,6419
3	CO₂, H₂O	1,167	0,143	0,342	0,3690	0,4099	0,4285	0,4553	0,4824
4	BF₃	1,111	0,1	0,236	0,2752	0,3085	0,3224	0,3462	0,369
5	SiF₄, CF₄, Al₂O₃	1,083	0,0766	0,213	0,2185	0,2462	0,2589	0,2782	0,2972

1) Gases; 2) thermal efficiency at various pres-
sures, in atm; 3) number of atoms in molecule; 4)
example.

$$u = \sqrt{\eta_t 2g \frac{k}{k-1} \cdot pv} \ \text{m/sec}; \qquad (3)$$

$$u = \sqrt{\eta_t 2g \frac{k}{k-1} \cdot RT} \ \text{m/sec}; \qquad (4)$$

$$u = 0{,}863 \sqrt{\eta_t \frac{k}{k-1} \cdot \frac{Hv}{C_p}} \ \text{m/sec}, \qquad (5)$$

where $\underline{p}$ is the pressure in the combustion chamber; $\underline{v}$ is the specific
volume of the gaseous products of combustion, i.e., the volume of the
gases formed in the combustion of 1 kg of propellant, referred to
standard conditions; T is the temperature at which the propellant-
combustion process takes place; R is the gas constant; C_p is the heat
capacity of 1 kg of products of combustion; η_t is the thermal effi-
ciency; $\underline{k}$ is the adiabatic exponent.

Equations (3), (4), and (5) are obtained by a modification of Eq.
(1), proceeding from the following well-known relationships in thermo-
dynamics:

$$H = C_p T; \quad pv = RT; \quad \frac{k}{k-1} = \frac{427 \cdot C_p}{R}.$$

With Formulas (1)-(5) it is possible, in approximate terms, to
estimate the exhaust velocity and specific thrust which can be obtained
with the given propellants, said estimate accurate to within ±2.5%, and

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it is also possible to estimate the parameters which change these factors.

Exact thermodynamic calculations of the processes of rocket-propellant combustion are discussed in corresponding literature sources [10].

Formula (5) is convenient for an evaluation of the exhaust velocities of the products of combustion of those propellants which result in the formation of solid particles, i.e., Al_2O_3, MgO, and BeO. This formula includes the heating value, the specific volume of the products of combustion, and the heat capacity of 1 kg of the gaseous, liquid, and solid phases of the products of combustion. The specific impulse can be obtained from the exhaust velocity of the products of combustion, if this value is divided by the force of gravitational acceleration.

The final efficiency of the propellant can be estimated in terms of rocket velocity and range, which are possible with the utilization of a given propellant.

K.E. Tsiolkovskiy [16], in his development of the mathematical theory for the motion of a rocket, derived a formula in which the maximum velocity of a rocket is associated with the exhaust velocity of the products of combustion and the relative weight and density of the propellant in the rocket:

$$V = u \ln \frac{G_p + wd}{G_p} \quad \text{or} \quad V = u \ln (1 + \gamma \cdot d)$$

and

$$V = g R_{y\pi} \ln \frac{G_p + wd}{G_p} \, ,$$

where G_r is the weight of the rocket, without propellant; $\underline{w}$ is the tank volume; $\underline{d}$ is propellant density; R_{ud} is the specific thrust; and γ is the index for rocket design w/G_r.

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This expression was derived without taking into consideration the force of terrestrial gravitation and air resistance. When terrestrial gravitation is taken into consideration, this expression takes the following form:

$$V = u \ln \frac{G_p + wd}{G_p} - \bar{g} \cdot t,$$

where t is the time to the instant of the complete burning up of the entire propellant; $\bar{g}$ is the average value of gravitational acceleration during time t.

The maximum velocity of a multistage rocket is determined by the following formula:

$$V = n \cdot u \ln [\sigma (1 - \lambda) + \lambda] - \bar{g} \tau_{akt},$$

where n is the number of stages; u is the exhaust velocity; σ is the structural parameter of the stage, i.e., the ratio of the weight of the empty stage to the weight of the fully loaded stage; λ is the co-efficient of payload, i.e., the ratio of the weight of the load for the given stage (i.e., the weight of the remaining stages of the rocket and the payload) to the weight of the stage under consideration; $\bar{g}$ is the average gravitational acceleration; τ_{akt} is the operating time for all engines.

The Tsiolkovskiy equation can be used for a comparative evaluation of propellant efficiency, since this equation provides a relationship between two propellant indexes such as the exhaust velocity associated with heating yield and propellant density.

The maximum altitude which can be attained by a rocket on vertical ascent, with terrestrial gravitation taken into consideration, is characterized by the following formula:

$$h = j \frac{u^2}{2g(g+j)} \left(\ln \frac{G_p + wd}{G_p} \right),$$

where h is the altitude of rocket ascent; j is the acceleration of the

- 39 -

rocket; $\underline{u}$ is the exhaust velocity of the products of combustion; $\underline{g}$ is the acceleration of gravity.

The altitude of rocket ascent is directly proportional to the heating value of the propellant. At low velocities, the flight range of a body launched from the Earth at an angle α to the horizon is determined by the following elementary formula:

$$S = \frac{u^2}{g} \sin^2 \alpha.$$

The range of the rocket cannot be found with sufficient accuracy by elementary calculations. Ye. Zenger [14, 15] presents range as a quadratic and cubic function of the exhaust velocity of the products of combustion, as well as the logarithm of the ratio of rocket weights with and without propellant:

$$S = \frac{u^2 \left(\ln \frac{G}{G_p} \right)^2}{2g\varepsilon} \tag{6}$$

and

$$S = K \cdot u^3 \left(\lg \frac{G_p + wd}{G_p} \right)^3,$$

where S is the range of the rocket; ε and K are coefficients; G is the starting weight.

All of the examined methods of evaluating the properties of a propellant with respect to flight range, velocity, and altitude of rocket ascent are not absolute but represent only the first steps in the attempt at a comparative evaluation of propellant quality. Apparently, the cubic function best reflects the change in range as a function of $\underline{u}$ and G/G_0.

The energy properties of a propellant for liquid reaction engines are determined by the following indices:

1) the heating yield of the propellant;

2) the elementary composition of the propellant, which is a func-

tion of the composition of the products of combustion, and consequently, by thermal efficiency as well;

3) the density of the propellant.

All three of these indices are totaled in a special manner and are reflected in expressions for rocket velocity and range.

The heating value and density of the propellant characterize flight range.

The possibility of using propellants, under actual conditions, is determined by their operational properties which can limit the application of propellants exhibiting good energy indices.

6. Area of Application of Liquid Reaction Engines

a) Military rockets

Liquid reaction engines have been used in a great variety of ways in rocket engineering and aviation during the past 15 years and are finding an ever increasing place for peaceful purposes, both scientific and technical.

Depending on the area of their application (rocket construction, aviation, naval forces), liquid reaction engines can be divided into the following types:

1) ZhRD rockets (rocket power plants);

2) aviation ZhRD (power plants for aircraft);

3) takeoff ZhRD (for aircraft takeoffs);

4) naval torpedo ZhRD (power plants for naval torpedoes, to propel these beneath the water);

5) auxiliary ZhRD for various areas of application.

In military matters, rockets have been used for a variety of tactical and strategic applications. Rockets are designated for a number of purposes:

1. The bombardment of industrial and administrative targets far
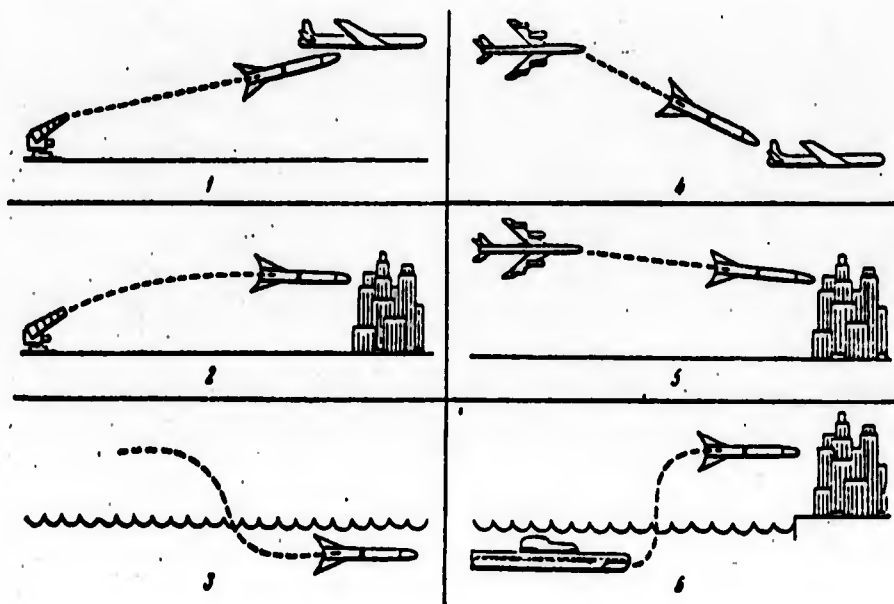
Fig. 15. Area of application of military rockets.
1) Attack against aircraft, from the ground
("ground-to-air"); 2) destruction of ground tar-
gets from the ground ("ground-to-ground"); 3) de-
struction of submarines from the air ("air-to-
water"); 4) destruction of aerial targets from
aircraft ("air-to-air"); 5) destruction of ground
targets from aircraft ("air-to-ground"); 6) de-
struction of ground targets from submarines
("water-to-ground").

behind and close to the front lines.

Rockets can be launched:

a) from specially equipped platforms behind the lines;

b) from the decks of naval vessels;

c) from submarines;

d) from aircraft which, in this case, need not fly all the way to
the target [14, 15, 18]; in these cases, the radius of rocket applica-
tion is increased.

2. Radio-controlled rockets are used for purposes of anti-aircraft
defense to protect important targets, vessels, etc. against air at-
tack.

3. Rockets which are controlled in their flight from another air-
craft are used by air forces to attack enemy aircraft, destroy tactical

Fig. 16. The launching of the
intercontinental ballistic
rocket — the "Atlas."

ground targets, naval vessels, etc.

The areas in which rockets can be employed for military purposes
are shown in Fig. 15.

Industrial mass production and utilization of rockets with liquid
reaction engines was begun in Germany, for the first time, in 1943-
1944. The first such rocket was the German A-4 rocket.

The A-4 rocket was a complex unit consisting approximately of
30,000 various component parts. The rocket was intended for the bom-
bardment of industrial and administrative centers. The rocket was 14

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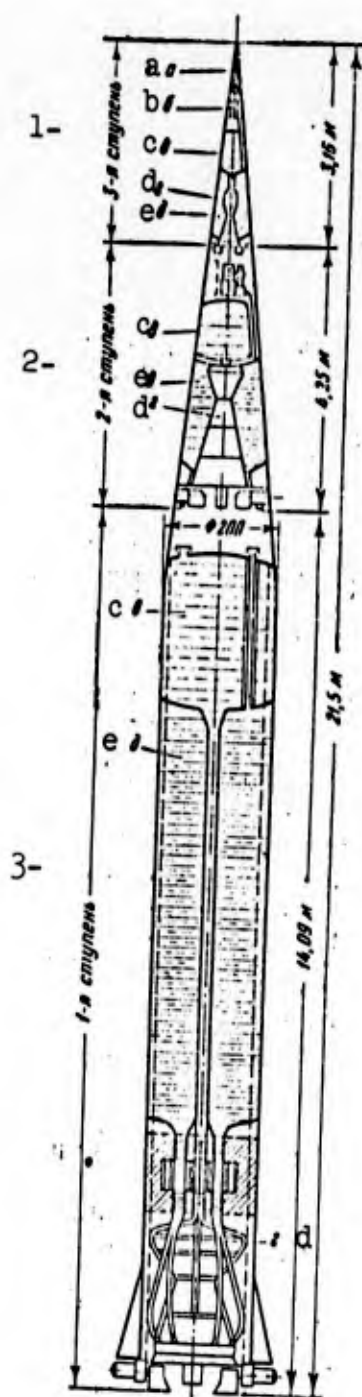
Fig. 17. Schematic diagram of
a three-stage rocket. a) Pay-
load; b) control instruments;
c) and e) fuel tanks; d) en-
gines. 1) 3rd stage; 2) 2nd
stage; 3) 1st stage.

meters long and had a diameter of 1.65 meters; its total weight came

to 12.9 tons of which the propellant — 75% ethyl alcohol and liquid

oxygen — made up 8750 kg, that is 67% of the total rocket weight. The

explosive charge, carried in the warhead, weighed 980 kg. The engine

operated, on the average, for 70 seconds, and the rate of propellant feed was 125 kg/sec; the total thrust produced by the engine was 27,200 kg. The propellant was burned during the active phase of the trajectory, equal to 30 km, at the end of which the rocket attained a velocity of 1500 m/sec, or 5000 km/hr. Subsequently, motion was due to inertia. The rocket covered a distance of 275 to 300 km in about 300 seconds; the high point of the trajectory was 80 km. In vertical ascent, the rocket was capable of attaining an altitude of 160 km.

During a period of seven months of the war (in 1944 and 1945) 1100 rockets were launched [13, 14, 15]. A gigantic underground factory, with a main tunnel some 2 km long, was built at Nordhausen (Germany) for the production of the A-4 rockets during the war. This factory was equipped with 25 thousand machine tools. There were some 30,000 workers employed at the factory.

The A-4 rocket, in its time (1944-1946), represented an outstanding technical achievement.

Contemporary rocket construction is developing along the lines of multistage long-range composite rockets (the launching of such a rocket is shown in Fig. 16). A composite rocket consists of several smaller rockets, each carrying independent engines. As the propellant is consumed, the first stage of the rocket is jettisoned, and the engine of the second stage is started; but this is not done until the rocket has attained its maximum velocity, developed by the first stage, etc. With this system, the maximum velocity and, consequently, the greatest range and altitude are possible. The basic design of a three-stage rocket is presented in Fig. 17. Multistage rockets have found application in contemporary engineering practice [18-24].

One of the trends of rocket construction is the work being done on the design of ballistic rockets having an effective radius of sev-

eral thousand kilometers.

In August of 1957, the Soviet Union, for the first time in history, launched an intercontinental multistage ballistic rocket.

The tests of the rocket were carried out successfully and they confirmed fully the validity of the calculations and the selected design.

The rocket flew at an extremely great altitude. Having covered a tremendous distance in a very short period of time, the rocket landed in its assigned target area.

The results that were obtained demonstrate that it is possible to launch a rocket from any region of the globe.

In 1960 and 1961 the Soviet Union tested new multistage ballistic rockets [25]. The launching was carried out from our country; the rockets landed in the assigned target areas of the Pacific Ocean, some 12 to 12.5 thousand kilometers from the launching site. The last stage was not an active stage, but rather a mockup. The next-to-last stage of the rocket, together with the mockup of the last stage, moved exactly along their calculated trajectory; a velocity in excess of 7 km/sec was attained.

The next-to-last rocket stage, having carried out its assignment, on reentry into the dense layers of the atmosphere at an altitude of some 80 to 90 km, was destroyed in its continued motion and partially burned up. The mockup of the last rocket stage, adapted to penetrate the dense layers of the atmosphere, reached the surface of the water close to the calculated point of impact.

Special vessels of the Soviet navy, positioned in the region of anticipated rocket impact, carried out valuable telemetric measurements during the descent leg of the flight trajectory.

On the basis of the measurements that were carried out it was es-

tablished that the deviation from the point of rocket impact from that calculated amounted to less than 2 km in 1960, and less than 1 km in the 1961 tests, thus confirming the great accuracy of the rocket control system [25].

There are long-range rockets in the Soviet Union that are intended for launching from submarines [8].

Soviet liquid rockets, shown during the First-of-May 1961 parade, are shown in Figs. 18 and 19.

Powerful multistage rockets are extremely important from the standpoint of the launching of satellites and space vehicles which are employed for purposes of investigating outer space.

The USA has a series of short-range rockets (50-600 km), medium-range rockets (2400 km), and intercontinental ballistic rockets (8000-10,000 km).

The characteristics of contemporary liquid ballistic USA rockets (1955-1961) are presented in Table 2.

TABLE 2

Characteristics of Contemporary Ballistic USA
Rockets with ZhRD [26]

1 Название	Дальность ракеты, 2 ^{км}	Стартовый вес, m 3	Длина, $м$ 4	Диаметр максимальный, $м$ 5	Тяга двигателя первой ступени, m 6	Максимальная скорость, $^{км/сек}$ 7
8 «Редстоун»	300—600	—	18	1,5	32	—
9 «Тор»	2 400	45	22,6	2,3	72,3	3
10 «Юпитер»	2 400	43	18	—	70	3
11 «Атлас»	10 000	90	24,4	2,7	120	4,5—5,5
12 «Титан»	8 800	90	36,5	3,04	136	—
13 «Сатурн»	*	580	56,5	6,5	684	>11,2

*Flights into outer space.

1) Name; 2) rocket range, in km; 3) launch weight, in tons; 4) length, in m; 5) maximum diameter, in m; 6) thrust of first-stage engine, in tons; 7) maximum velocity, in km/sec; 8) "Redstone"; 9) "Thor"; 10) "Jupiter"; 11) "Atlas"; 12) "Titan"; 13) "Saturn."

The "Atlas" rocket was designed for a range of 8000 to 10,000 km. The high point of the trajectory of this rocket lies between 980 and 1280 km. The power plant consists of three engines. The sustainer engine, developing a thrust of 61 tons, was designed to operate for a period of 180 seconds. Two boosters, each developing a thrust of 45.3 tons, are jettisoned after the propellant has been exhausted -- these boosters form a cluster with the sustainer rocket. It was reported in 1959 that the accuracy of the USA rockets was characterized, for a range of 8000 km, by a deviation of ±16 km from the target point [26].

Of the new powerful USA rockets mention should be made of the "Saturn" rocket system developed in the USA.

Plans called for the completion of the hot-firing tests of the first stage of the "Saturn" rocket in 1960; this rocket is designed to carry a payload of 20 tons into orbit and the total initial weight of the system is 545 tons. Thus the payload amounts to 4%. The first stage of the "Saturn" rocket is a cluster of 8 ZhRD [liquid rocket engines] developing a total thrust of 684 tons, i.e., each ZhRD develops a thrust of 95.5 tons. The upper stages will carry from three to five engines, using liquid hydrogen as the propellant.

The first stage of the "Saturn" rocket, whose launching with a mockup was scheduled for the first half of 1961, is 25 meters long and has a diameter of 6.6 m. The first-stage engines operate on RP-1 kerosene and liquid oxygen.

The version of this rocket with three stages, has an over-all length of 56.5 m.

The four engines of the second stage, developing a total thrust of 364 tons, and the two engines of the third stage, developing a thrust of 152 tons, operate on liquid oxygen and liquid hydrogen.

The "Saturn" system, designed to fly to the Moon and land on its
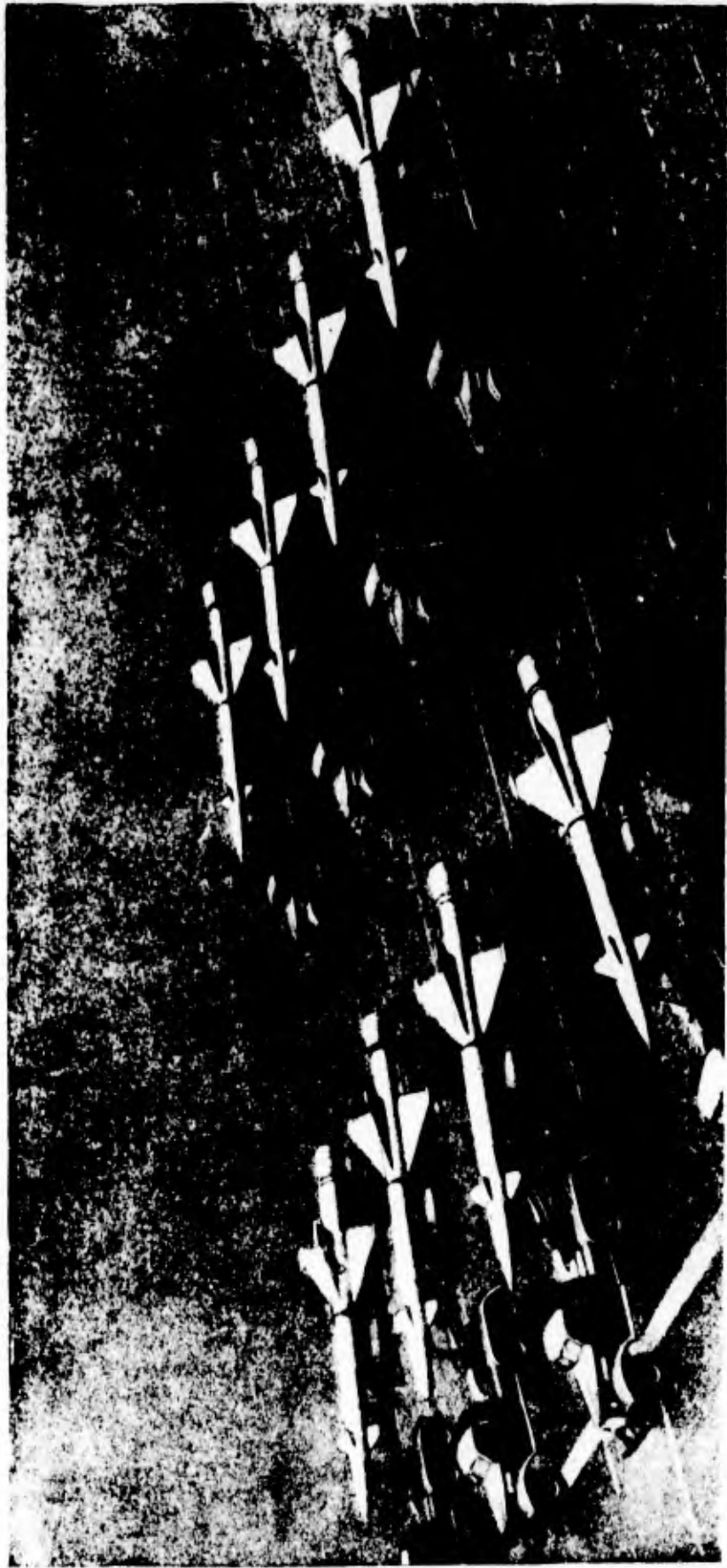
Fig. 18. Soviet rocket equipment.

Fig. 19. A Soviet liquid rocket.

surface, will be ready by 1963-1964.

Plans call for the development of the "Nova" rocket system by 1967; the first stage of this system will consist of several engines developing a total thrust of between 2700 and 4000 tons.

This rocket system will be capable of landing people on the Moon without any intermediate refueling in its orbit.

Plans call for a version of the "Nova" rocket, having a launching weight of 1100 tons, based on existing rockets.

The booster stage will consist of seven tanks of the "Titan" rocket and two ZhRD "F-1" engines, developing a total thrust of 900 tons, said engines operating on liquid oxygen and kerosene. The second stage will include three tanks of the "Titan" rocket, and these tanks will be used to supply a single engine developing a thrust of 225 tons. An interesting point is the fact that the plans call for the use of turbojet and ramjet engines to accelerate these heavy rocket systems to altitudes of 15-20 km; the jet engines will produce velocities up to 1200 m/sec. Through the utilization of the booster VRD it will be possible to increase the payload.

In rocket versions involving the use of nuclear engines, which the USA plans to introduce in 1970-1975, the initial acceleration of the system is to be carried out by means of several TRD mounted on a carrier moving over inclined (upward) guide rails for a distance of 24 km. During this acceleration stage, the velocity will reach 600 m/sec, after which the direct-flow [ramjet] engines on the vehicle will be started, and these will provide acceleration up to 3000 m/sec, after which the nuclear engine is to be turned on, permitting entry into the given orbit. The specific impulse of the nuclear engine will be of the order of 1500-3000 seconds.

The designers are presently concerned with the utilization of air-reaction engines for the acceleration of space systems to altitudes of 15-20 km. The weight of a passenger space vehicle will be 50,000 to 80,000 tons, and this is equivalent to the weight of ocean liners. Space vehicles of such great weight will take off from and land on water.
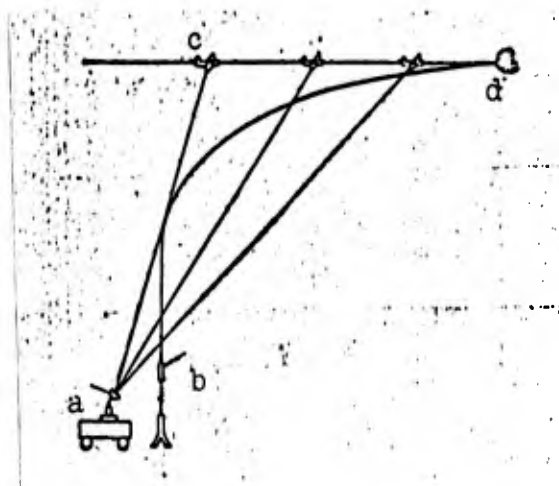
Fig. 20. Operating diagram of a radio-controlled anti-aircraft rocket. a) Radar; b) rocket; c) aircraft; d) destruction of aircraft.

In addition to the long-range rockets, small·ZhRD rockets have been developed for the Army to operate over a range of 50 to 120 km,

and these rockets can be employed by ground forces for tactical purposes.

A new area in the utilization of rockets is their application to anti-aircraft defense.

Contemporary radio-controlled anti-aircraft rockets have been developed for purposes of protecting industrial and administrative centers against air attacks [18-27]. An operating diagram of a radio-controlled rocket is presented in Fig. 20.

Figures 21-24 show an anti-aircraft rocket on its launching installation, the launching of the rocket, its approach to the aircraft, and the destruction of the aircraft.

There are several types of radio-controlled anti-aircraft rockets in the USA.

For example, the "Nike-1," the first rocket of this type produced in 1952, has a solid-propellant booster and a liquid-propellant sustainer engine; this rocket is capable of destroying a target up to an altitude of 18 km. Then came the improved "Nike-Ajax" rocket, and in 1958 it was proposed that the anti-aircraft defense rocket "Nike-Ajax" rocket be replaced by the "Nike-Hercules" missile. The launching weight of the latter is 5000 kg, it is 11.9 m long, has a range of 110-120 km, it can attain an altitude of 21 km, it has a solid-propellant engine, and a warhead charge weighing 100-150 kg. A single "Nike-Hercules" missile costs $15,000, and the fire-control station costs $500,000.

The "Nike-Zeus" is a similar missile which has a range of 160 km and can destroy a target at an altitude of 15 to 25 km. This missile has an engine operating on a solid propellant based on ammonium nitrate and a polysulfide; the engine is uncooled, and operates for a period of 30 to 60 seconds. Engine reliability is achieved by the utilization

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of new shielding heat-insulating materials — liners that burn up, inserts made of glass-filled textolite (resin-impregnated laminated cloth), etc.

The Soviet Union also has radio-controlled anti-aircraft rockets. The first military application of a rocket of this type occurred on 1 May 1960 when a single rocket was used, in the vicinity of the city of Sverdlovsk, to shoot down the "U-2" reconnaisance aircraft at an altitude of 20 km.

Rocket engines can also be used in aviation.

Solid- and liquid-propellant rocket engines in aviation are used as boosters. The greatest power is needed during the takeoff of an aircraft; during its motion through the air the aircraft requires less power, and therefore the use of boosters which increase the total thrust for short periods of time makes it possible to accelerate the takeoff of an aircraft by a factor of at least two, thus permitting a reduction in the length of the runway, as well as making it possible to take off from the deck of a vessel. Boosters also make it possible to increase the payload of an aircraft by 20%, and velocity can also be increased for short periods of time in the air through the use of rocket boosters.

By the end of the Second World War, the German firm "Walther" began production of boosters with ZhRD capable of developing thrusts of 500, 1000, and 1500 kg. Engines of this type are now being produced in Great Britain and other countries.

Aircraft with ZhRD have been designated as rocket aircraft. The first rocket aircraft with a ZhRD was the Me-163 fighter which appeared in Germany at the end of the war. This fighter had a maximum velocity of 960 km/hr which was extremely great for that time, and it was capable of climbing to an altitude of more than 13,000 meters. The

Fig. 21. An anti-aircraft radio-
controlled rocket on its launch-
ing installation.
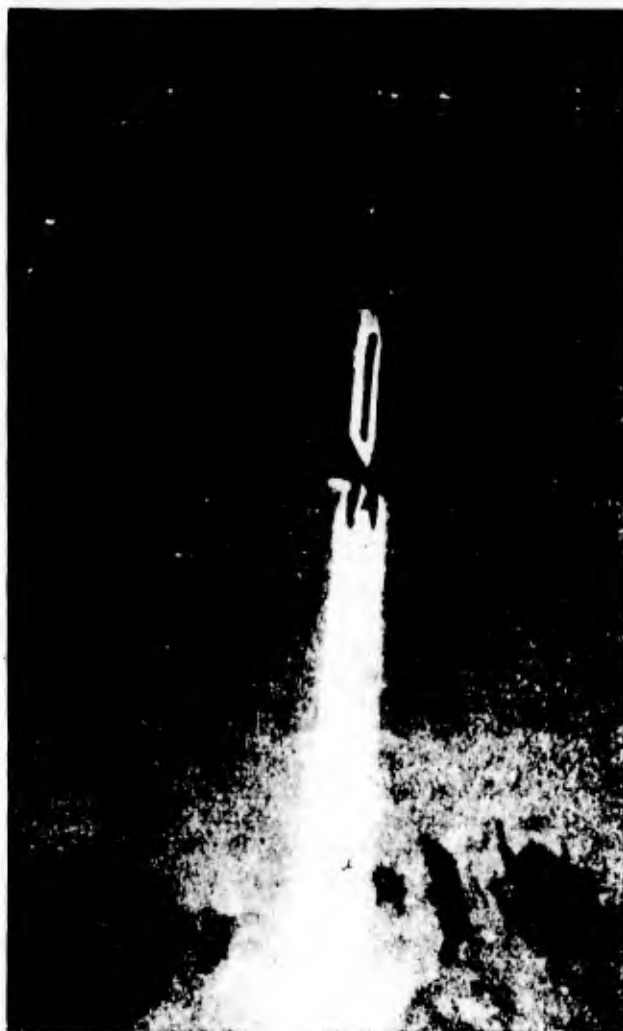
Fig. 22. The launching of an anti-air-
craft rocket.

Fig. 23. Approach of anti-air-
craft rocket to aircraft.

Fig. 24. Destruction of aircraft
on explosion of rocket.

greatest thrust developed by this engine was 1500 kg. The fuel supply

lasted only for 8 minutes; however, during this period of time a

single rocket fighter was capable of shooting down several heavy

bombers, in defense of major industrial centers.

In 1954-1955, flight tests of a series of liquid reaction air-

craft were conducted abroad. For example, the "Screamer" engine (USA),

intended for supersonic aircraft, operates on liquid oxygen and kero-

sene and develops its maximum thrust of 4000 kg at an altitude of 12.2

km.

Aircraft with rocket engines have not come into widespread use

because of the limited flight duration. However, such aircraft are necessary for special purposes (fighter-interceptors). A velocity of about 3000 km/hr and an altitude of 27,400 m were attained with a rocket aircraft in 1955. In 1956, flight tests were conducted with an experimental rocket aircraft which had an eight-chamber ZhRD capable of developing more than 4 tons of thrust; this aircraft was designed to fly at a velocity of about 4000 km/hr [28]. There are jet aircraft which are equipped with rocket and turbojet engines.

Fig. 25. English supersonic jet aircraft with a single rocket or two turbojet engines.

Fig. 26. Soviet supersonic aircraft with rocket and air-reaction engine.

In 1961, in the Soviet Union a high-altitude flight record (34.7 km) was established with an aircraft which had a rocket engine; this aircraft was shown at an air show in 1961.

Figures 25 and 26 show jet aircraft behind which the gas stream of a rocket engine is clearly visible.

b) Rockets for the launching of satellites and space vehicles

Rockets and rocket engines are finding ever increasing application for peaceful purposes [29] and for scientific investigations. Rockets are widely used to study the upper layers of the atmosphere at altitudes from 25 to 450 km, as well as for biological investigations. Both in the USSR and abroad, animals have been sent up in rockets in order to study their behavior under conditions of space flight. Rockets have been used to conduct aerial photography of the Earth from great altitudes. Rivers, cities, highways, railroads, etc., can be recognized on photographs taken at altitudes of 90-100 km. There are photographs of the Earth, taken at altitudes of 170-225 km, which cover a surface area of some 5000 km. Mountain relief, the curvature of the Earth's surface, etc., can be seen on these photographs.

The outstanding scientific achievement in recent years, beginning with 1957, is the launching of the artificial Earth satellites and space rockets, and this was first done in the Soviet Union [30] and later on in the USA.

On 4 October 1957, the USSR launched successfully the first artificial satellite of the Earth. An intercontinental rocket was used for this purpose.

The rocket carried the satellite of the Earth into orbit and imparted to the satellite a velocity of 8 km/sec. This terrestrial satellite and the rocket entered into an elliptical trajectory (orbit) around the Earth. The Earth satellite flew at altitudes of up to 900

km and completed a single revolution every hour and thirty five min-
utes during the first days after launch. The satellite was in the
shape of a sphere, with a diameter of 58 cm, and it weighed 83.6 kg.
Radio transmitters, continuously emitting radio signals, were in-
stalled aboard this "sputnik."

The successful launching of the first artificial satellite of the
earth designed by man offered a tremendous contribution to the treas-
ures of the world's science and culture. This scientific experiment
was of tremendous importance from the standpoint of knowledge about
cosmic space as well as from the point of view of studying the Earth
as a planet of our solar system.

On 3 November the Soviet Union launched the second artificial
satellite of the Earth. The second artificial satellite, made in the
USSR, was the last stage of the rocket which carried containers with
scientific equipment and an experimental dog. The total weight of the
equipment, the experimental animal, and the electric power sources
came to 508.3 kg. The satellite attained an orbital velocity in excess
of 8000 [sic] km/sec. The satellite reached a maximum distance from the
earth of about 1700 km; it completed a single revolution, initially,
in 1:43 hours. On the basis of measurement data obtained from this
satellite, the operation of the scientific equipment and the monitor-
ing of the ability of the animal to survive proceeded in normal fashion.

Soviet scientists expanded their investigation of outer space and
the upper layers of the atmosphere through the launching of the second
artificial satellite of the earth, which contained scientific equip-
ment and an experimental animal.

On 15 May 1958, the third Soviet artificial satellite of the
earth was launched by means of a multistage rocket; the weight of the
satellite, after separation of the last rocket stage, came to 1327 kg.

The height of the orbit above the surface of the Earth varied between 266 and 1880 km; the time required for a complete revolution, during the initial period, was 105 minutes. Scientific equipment weighing 968 kg was installed aboard the satellite; this equipment made it possible to conduct various experiments and investigations. A multichannel telemetry system with high resolving power was installed on the satellite in order to transmit scientific observation data to ground recording stations. The third artificial satellite of the Earth continued its orbital motion for almost two years and completed more than 10,000 revolutions around the Earth.

On 16 March and 26 April 1962 the Soviet Union launched an additional four satellites of the Earth.

During the period from the beginning of 1958 through March 1961 the USA launched several tens of satellites which carried scientific equipment weighing from 4.5 kg to several tons. The launching of the first artificial satellite of the Earth from the USA took place on 31 January 1958 and was accomplished with a medium-range "Jupiter-C" Army rocket. The last stage of the rocket carrying the satellite weighed 14 kg without propellant.

The later satellites launched by the USA carried television equipment for transmission of images of the Earth's surface over which the satellites passed. As an example of this type of satellite we can cite the USA satellite "Tiros," launched in 1960; this satellite transmitted television images of the Earth's surface from altitudes ranging between 725 and 1300 km. Satellites of this type may be employed for military reconnaisance purposes. New types of propellants were employed by the USA for the launching of artificial Earth satellites; we have reference here to dimethyl hydrazine with oxygen, as well as solid propellants.

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The launching of artificial Earth satellites made possible the accumulation of experience in preparation for space flights and the development of new and more powerful multistage rockets, rocket-control systems, and improvements in the scientific equipment aboard these satellites.

As a result of all of this, on 2 January 1959 the Soviet Union successfully launched the first multistage rocket in the direction of the Moon [31]. The last and guided stage of the rocket exceeded the second cosmic (escape) velocity of 11.2 km/sec at which a rocket can escape the field of terrestrial gravitation and move away forever from the Earth.

After all of the propellant had been consumed, the weight of the last stage amounted to 1472 kg, including the payload of the rocket, which weighed 361.3 kg and included various instruments and two radio transmitters. A portion of the payload is situated directly in the frame of the rocket, and the other part is housed in a hermetically sealed container which is separated from the last stage after cessation of engine operation.

In order to reach the designated area on the Moon, a strictly calculated trajectory must be maintained; the velocity of the rocket at the end of the acceleration phase must exhibit a deviation of no more than 0.5% (i.e., 56 m/sec at a velocity of more than 11.2 km/sec) from the set velocity, and the deviation from the required heading must not exceed 0.5°. All of the scientific information obtained by the measuring instruments was transmitted by means of the radio transmitters which operated on a frequency of 19.993 and 183.6 Mc. In commemoration of the first space rocket produced by the Soviet Union, the container held two pennants showing the State Seal of the Soviet Union. Radio communications with the rocket were maintained in outer space to

a distance of 500,000 km. After a period of 35 hours after the launching, the cosmic rocket had come to within 5000-6000 km from the lunar surface, having covered a distance of more than 370,000 km. By 7-8 January 1959 the rocket had passed beyond the gravitational field of the Earth and covered a distance of more than 930,000 km. Virtually free of the effect of terrestrial gravitation, the rocket entered an elliptical orbit around the Sun, becoming a satellite of the Sun. The duration of a single revolution of this first Soviet artificial planet about the Sun is 15 months, with the perihelion at 146 million and the aphelion at 197 million kilometers with respect to the Sun.

The mockup of the last stage of the Soviet cosmic rocket is presented in Fig. 27.

After the first Soviet cosmic rocket, on 3 March 1959 the USA launched a four-stage rocket, the "Pioneer IV," in the direction of the moon; this rocket had a launch weight of 60 tons (Fig. 28). The first stage consisted of a medium-range "Jupiter" ballistic rocket which operated on a liquid propellant, and the engine produced a thrust of 68 tons; the second stage consisted of a cluster of eleven solid-propellant "Sergeant" rockets having a total weight of 327 kg; the third stage consisted of three such rockets, weighing 94 kg; the fourth rocket consisted of a single solid-propellant rocket weighing 27 kg. The container carrying the instruments, which separated from the fourth stage, weighed 6 kg, i.e., 0.01% of the launching weight.

On 12 September 1959 the Soviet Union launched the second cosmic rocket to the Moon. The launch was accomplished by means of a multistage rocket. The engines of this rocket operated for several minutes on a propellant which exhibited high heating value. By the time the engine of the last stage ceased operation, the rocket had accelerated to a velocity in excess of the second cosmic (escape) velocity — 11.2

km/sec, and the last stage with the container and scientific equipment was in orbit. The last stage of the rocket was a guided rocket which weighed 1511 kg without propellant. It carried a container which housed scientific equipment weighing 390.2 kg. On its way to the Moon the rocket continuously lost speed as a result of the effect of terrestrial gravitation and its velocity dropped to 2 km/sec; subsequently, as the rocket encountered the gravitational force of the Moon, the velocity began to increase and attained 3.3 km/sec.

Fig. 27. Mockup of the last stage of the Soviet cosmic rocket.

The cosmic rocket (the container with equipment and the last stage), launched on 12 September 1959, reached the surface of the Moon on 14 September at 00:02:24 hours, Moscow time, having covered a distance of 371,000 km. The container with its scientific instruments was landed on the Moon, at a point approximately 800 km from the center of the visible disk of the Moon, i.e., the rocket's target. The launching of a rocket to the Moon is an extremely complex scientific and technical problem. In order to carry out a flight to the moon it was necessary to devise a highly perfected multistage rocket, powerful rocket

engines operating on propellants exhibiting high heating value, and in addition it was necessary to produce an extremely exact rocket-flight control system, ground launching equipment, and a complex of automatic measuring equipment for purposes of observing the rocket flight. Theoretical investigations and technical calculations preceded the launching of the rocket to the Moon; these activities made it possible to determine the trajectory parameters and the time of launch which would ensure the successful solution of the problem of attaining the surface of the Moon under the most favorable of conditions.

On 4 October 1959 the Soviet Union launched the third cosmic rocket, and this rocket carried an automatic interplanetary station.

This launching was carried out by means of a multistage rocket whose last stage, having attained the given velocity, placed the automatic interplanetary station into its required orbit. The orbit of the automatic interplanetary station was selected so as to provide for the passage of the station close to the Moon and to fly around the Moon and return to Earth. A velocity somewhat less than the second cosmic (escape) velocity was needed at the end of the acceleration sector in order to accomplish this. The last stage of the cosmic rocket weighed 1553 kg without propellant, and this includes the weight of the automatic interplanetary station (278.3 kg) and the weight of the measuring instruments and power sources (156.5 kg) housed in the last stage of the rocket. Thus the total weight of the payload amounted to 434.8 kg, and the weight of the last stage of the rocket, without propellant and scientific equipment, came to 1118.2 kg.

The purpose of the launching of the third cosmic rocket was to resolve a number of problems dealing with the investigation of outer space. The most important of these problems was the obtaining of a photographic image of the surface of the Moon and, in particular, of

Fig. 28. The launching of a
multistage rocket in the USA
to the moon.

the invisible side of the moon. The automatic interplanetary station
is a space flying craft equipped with complex radio-engineering, photo-
television, and scientific equipment, a special orientation system,
program control devices for the functioning of the on-board equipment,
an automatic control system to maintain the thermal regime within the
station, and electric power sources. The phototelevision equipment of
the station made possible the automatic photography of the reverse
side of the Moon, the processing of the film, and its preparation for
transmission of the image back to Earth. After a period of 32 hours,
the cosmic rocket reached the vicinity of the Moon and passed within a
distance of 7000 km from the lunar surface, bending around the Moon,

and then through the action of terrestrial gravitation again began its approach to Earth. On its return to Earth in its first revolution, the interplanetary station passed at a distance of 47.5 thousand kilometers from the center of the Earth.

On 7 October the interplanetary station carried out its task of photographing the back side of the Moon. The time required for the photography process was selected so as to position the station, in its orbit, between the Moon and the Sun which, at that time, was illuminating approximately 70% of the invisible side of the Moon. At this time, at the beginning of the photography process, the station was some 65.2 thousand km from the lunar surface, and at the end of the photography process its distance from the Moon's surface was 68.4 thousand km. By means of a special command emitted by the orientation system, the station was turned so that the objectives (lenses) of the camera were directed at the back side of the Moon, and the orientation system emitted the command to switch on the photo equipment. The photography of the Moon continued for approximately 40 minutes. At the completion of the photography phase, the film was transported into an automatic processing device where it was developed, fixed, and dried. The film was then placed into a special cassette for the transmission of images. The transmission of the lunar images was carried out on a command from Earth, at which point the power source for the on-board television equipment was switched on, the television equipment was connected to the on-board transmitters, and the film was drawn through. The signals of the television image, received by ground stations, were recorded by a variety of equipment. The signals of the lunar images were recorded on film by means of special equipment designed to record television images, as well as on magnetic tape recorders, and devices capable of recording images on paper.

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Fig. 29. Photograph of the invisible
side of the Moon.

The photographs showed the surface of the Moon that is not visible from the Earth, and there were pictures also of a small region with known formations. The presence on the photographs of a part of the Moon which had already been studied made it possible to relate newly discovered points to areas that were already known, thus determining their coordinates.

Figure 29 shows a photograph of the reverse side of the Moon.

Thus after 350 years of telescopic observations of the Moon, the reverse side of the moon was placed under observation for the first time.

At the station's maximum distance from the earth, the received part of the power of the on-board transmitter is lower by a factor of 100 million than the power received by a conventional television receiver. In this connection, for superlong transmissions of images in the case of extremely low radio-transmitter power, use was made of an

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image-transmission speed that was lower by a factor of tens of thousands than the transmission speed for conventional television broadcast centers.

By means of the radio-television equipment aboard the automatic interplanetary station, it was possible to transmit the images from various distances, even out to a distance of 470,000 km, thus confirming experimentally the possibility of transmitting images of high clarity in outer space over superlong distances.

The next step in the penetration of the depths of outer space was the launching of the Soviet cosmic rocket to the planet Venus on 12 February 1961, which is a stage in the study of the other planets of the solar system.*

A new principle was applied here in order to send a cosmic device on a trajectory to Venus — the launching of a guided cosmic rocket from on-board an artificial satellite of the Earth. In order to carry out this complex task, it was necessary to devise automatic orientation systems, and it was also necessary to design special devices capable of executing a given cosmic-rocket maneuver during orbital flight with great precision; for example, rocket deceleration, flight-trajectory correction, etc. The advantages of this new launching method for cosmic rockets are quite significant. For example, the motion of the satellite is kept under observation and the parameters of the satellite's orbit are determined with great accuracy from computer stations on the ground. This means that it will be possible to take into consideration accurately any errors in the insertion of the satellite into its orbit and to neutralize these errors during the launching of the space vehicle from the satellite, which is something that cannot be done when the interplanetary station is launched directly by means of a multistage rocket. All of this is of great significance for

the launching of a cosmic rocket to Venus, since it is considerably more difficult to reach the vicinity of Venus than to enter the gravitational field of the Moon.

The cosmic rocket was launched from the satellite at a preset point in the orbit. As the flight velocity of this rocket, with respect to the earth, exceeded the second cosmic (escape) velocity by 661 m per second and the rocket had passed a preset point in space, the rocket engine was turned on, and the automatic interplanetary station separated from the rocket and began its free flight on a trajectory to the planet Venus. The weight of the automatic interplanetary station, without the space rocket, amounted to 643.5 kg; the length of the automatic interplanetary station was 2.035 m and its diameter was 1.05 mm. Thus the launching of a guided device from on-board an artificial satellite of the Earth along an interplanetary route was carried out for the first time.

The ability of the Soviet Union to develop large and heavy artificial satellites of the Earth and the successful testing of powerful rockets capable of placing a satellite weighing several tons into a given orbit have made it possible to undertake the construction and testing of space vehicles for extended manned flights into outer space.

In the period from May 1960 through March 1961 the Soviet Union launched several space vehicles into an orbit around the Earth by means of powerful multistage rockets [32].

The weight of the first satellite vehicle, without the last stage of the rocket, came to 4.54 tons. A hermetically sealed cabin carrying a load simulating the weight of a man was carried on this satellite vehicle; in addition this vehicle carried all of the equipment necessary for the forthcoming flight of man into outer space; the weight of the various equipment came to 1477 kg. At a command from the Earth,

the hermetically sealed cabin, weighing 2.5 tons, was separated from the satellite vehicle.

The launch was intended to test and verify the various systems of the satellite vehicle which ensure safe flight, provide flight control, and work out the conditions required for a manned flight. All of the necessary information about the flight and functioning of the vehicle were transmitted by means of radio signals to Earth.

On 19 August 1960, from the territory of the Soviet Union, the second cosmic satellite vehicle with an experimental animal aboard was successfully launched. The satellite vehicle weighed 4.6 tons without the rocket, and its orbit varied between 306 to 339 km above the Earth. Upon completion of the investigation program, calculated to last a 24-hour period, and after the receipt of data on the functioning of the animals, a command was issued to bring about the descent of the vehicle from its orbit. The command was issued during the 18th orbit, exactly 24 hours after the launch, and the reverse-thrust rockets were then actuated, and these functioned with great accuracy, causing the satellite vehicle to leave its initial orbit and, because it was equipped with special heat shielding, safely pass through the dense layers of the atmosphere. After the actuation of the reverse-thrust rockets, the cabin flew some 11,000 km on its descent phase and was decelerated in the atmosphere by means of a special deceleration system. The satellite vehicle and the capsule separated from it at an altitude of 7 km and the capsule containing the experimental animal landed safely by means of a parachute at the designated point in the Soviet Union. The deviation of the landing point, from that calculated, was about 10 km.

Thus for the first time in the history of mankind live beings — a dog, mice, etc. — had spent more than 24 hours in space flight, cov-

ering in excess of 700,000 km, and they returned safely to Earth.

The Soviet Union soon launched a third and fourth satellite ve-
hicle.

On 4 February 1961 a heavy artificial satellite of the Earth,
weighing 6483 tons, was placed into orbit by means of an improved mul-
tistage rocket.

The fourth and fifth satellite vehicles, each weighing about 4.7
tons without the last rocket stage, were launched in March 1961. The
basic task of these launchings was the continued testing of the design
of the satellite vehicle and the instruments and systems installed
aboard, which were to ensure the ability of a man to withstand flight
in outer space. The vehicle again carried a dog and other biological
specimens.

c) The flight of man into outer space [33]

The launching of artificial satellites during a period of a num-
ber of years, and the return of these satellites to Earth, the launch-
ing of cosmic rockets, and the development of powerful rockets for
these purposes, laid the groundwork for a manned flight into the cos-
mos.

This historic event occurred on 12 April 1961 when Major Yuriy
Gagarin, for the first time in the history of mankind, completed his
outstanding achievement of flying around the terrestrial globe aboard
the Soviet space vehicle "Vostok."

The space vehicle with Yu. Gagarin weighed 4725 kg without the
last stage of the rocket, and this vehicle was placed into orbit
around the Earth with its altitude varying between 181 and 327 km. A
multistage rocket with six first-stage engines was used to place the
vehicle into orbit; the first-stage engines developed a total power
of 20,000,000 horsepower. Upon completing one revolution around the

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Earth, the vehicle was landed exactly at its designated point. The launch took place at 9:07 hours, Moscow time, and the automatic orientation system of the vehicle was switched on at 9:51 hours, and subsequently the reverse-thrust rockets were actuated at 10:25 hours, at which time the vehicle shifted from its orbit as a satellite of the Earth to its descent trajectory. At 10:55 hours the vehicle landed at its designated area in Saratov Oblast (Region). From the instant that the reverse-thrust system was actuated to the instant of descent, the vehicle covered approximately 8000 km which took approximately 30 minutes. During the landing phase, at an altitude of about 7 km the cosmonaut together with his couch was catapulted out of the capsule and Yu. Gagarin landed by means of a parachute, although the landing of the cosmonaut could have been carried out in the space capsule.

The flight of Yu. Gagarin demonstrated the reliability and high degree of accuracy, as well as the fail-proof functioning of both the rocket and the space vehicle. It was demonstrated that man can withstand normally the conditions of cosmic flight: during the entry into the orbit, in a state of weightlessness, and on the return to Earth.

On 6 August 1961 the Soviet Union launched the second cosmic vehicle, the "Vostok-2," into an orbit around the Earth; this vehicle was piloted by Major German Titov. The weight of this satellite vehicle, without the last stage of the rocket, came to 4731 kg. The vehicle was placed into an orbit close to that calculated, with its minimum distance from the Earth at 178 km and a maximum distance of 257 km. The initial period of satellite-vehicle revolution amounted to 88.6 minutes. German Titov successfully completed a 25-hour flight around the Earth and after carrying out the assigned program of investigation successfully landed on the territory of the Soviet Union close to the point of landing of the space vehicle "Vostok-2." The

Fig. 30. Photograph of the Earth, taken
from a high-altitude rocket.

space vehicle "Vostok-2" flew more than 17 times around the globe,
covering a distance in excess of 700,000 km.

The tasks of the flight were the following: to investigate the
effect on the human organism of an extended flight in an orbit around
the Earth, the investigation of man's ability to function and to carry
out all life functions under conditions of weightlessness. For scien-
tific observations in cosmic space, the space vehicle was equipped
with scientific apparatus, as well as with a television system which
made it possible to maintain two-way communications.

The flight of the space vehicle "Vostok-2" made it possible to
carry out extremely valuable scientific observations and demonstrated
that man can function normally during an extended flight in outer
space and to monitor a space flight, including the actual control of
the vehicle [34]. In his flight in orbit around the Earth, G.S. Titov
took photographs of the surface of the Earth.

Figure 30 shows a photograph of the Earth taken from a high-
altitude rocket.

Over a period of a number of years, the USA launched a number of
ballistic rockets vertically and along a ballistic curve to altitudes

ranging from 200 to 1200 km and these rockets carried animals for the purpose of studying the effect of cosmic space on the life functions of organisms.

At the beginning of May 1961, the USA launched a man — Captain A. Shepard — along a ballistic trajectory in a special capsule weighing 1500 kg, which was adapted to the ballistic "Redstone" rocket. This flight lasted 15 minutes and covered a distance of 500 km. The capsule carrying the pilot separated from the rocket at the high point of its trajectory, and it landed in the waters of the Pacific Ocean [sic].

On 20 February 1962 the USA launched the space vehicle "Friendship-7" into an orbit around the Earth; the pilot of this vehicle was John Glenn. The launch was carried out by means of a multistage "Mercury-Atlas-6" rocket system. The space vehicle weighed about 2 tons and completed four [sic] revolutions around the Earth and landed in the Atlantic Ocean. The vehicle completed one revolution around the Earth in 89 minutes, in an orbit ranging between the altitudes of 160 and 256 km.

The Soviet cosmonauts Yu.A. Gagarin and G.S. Titov have shown man the way into outer space; in the near future, mankind may anticipate flights of space vehicles to the moon and to the near-by planets of the solar system.

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[Footnotes]

Manu-
script
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No.

36   Structurally, a nozzle may be made to such dimensions that P_0 would be close to atmospheric pressure at great altitudes.

67   The following are the closest planets to the earth: Venus, with an average distance of 108.1 million km from the sun; Mars, 227.8 million km; and Mercury, 57.9 million km; the earth is situated at an average distance of 149.5 million km from the sun. The other larger planets of the solar system are 777.8 (Jupiter) and 5929 million km (Pluto) from the sun.

[Transliterated Symbols]

19	$G_B = G_v = G_{vozdukh} = G_{air}$
19	$G_T = G_t = G_{tiplivo} = G_{fuel\ (propellant)}$
19	$T_{rop} = T_{gor} = T_{goreniye} = T_{burning\ (combustion)}$
19	$T_{сопл} = T_{sopl} = T_{soplo} = T_{nozzle}$
20	$T_{cr} = T_{sg} = T_{sgoraniye} = T_{sombustion}$
21	$R_{уд} = R_{ud} = R_{udel'naya} = R_{specific}$
23	$\eta_п = \eta_p = \eta_{poletnyy} = \eta_{flight}$

24	$G_{\text{сам}} = G_{\text{sam}} = G_{\text{samolet}} = G_{\text{aircraft}}$
39	$\tau_{\text{акт}} = \tau_{\text{akt}} = \tau_{\text{aktivnyy}} = \tau_{\text{active (operating)}}$
39	$G_{\text{p}} = G_{\text{r}} = G_{\text{raketa}} = G_{\text{rocket}}$

Chapter 2

GENERAL CHARACTERIZATION OF TURBOJET FUELS AND
HYDROCARBON FUELS FOR ROCKET ENGINES

During the Second World War, jet engines and jet fuels underwent intensive development.

At that time, jet-engine fuels differed essentially from rocket-engine fuels, where alcohols and amines had previously been used exclusively.

Subsequently, gas-turbine kerosenes and later kerosenes developed specifically for rocket engines came into use in rocket engineering.

At the present time, it is difficult to draw a definitive boundary between gas-turbine kerosenes and rocket-engine hydrocarbon fuels. The latter differ from the former in their higher degree of purification and more distinct fractional composition, and in certain cases include unsaturated hydrocarbons or represent synthetic hydrocarbon products of a naphthenic character.

Let us examine rocket-fuel specifications.

1. Specifications for Rocket Fuels

As a result of research carried out over the last few decades, a series of fuels have been developed on the basis of direct-distillation petroleum products and thermal and catalytic cracking for air-breathing reaction-thrust engines. One of the essential requirements made for turbojet fuels is the possibility of producing them in very large quantities to satisfy the demands of aviation. According to certain foreign authors [1], the production of jet fuels during wartime may account for

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as much as 20 to 25% of petroleum production.

Prior to 1957, less than 3-4% of the petroleum extracted was processed into jet fuel for jet aircraft in the USA [2, 4].

In recent years, the following quantities of jet fuels have been produced in the USA (in millions of tons) [2, 3]:

1950 1,300	1959 18
1953 4,525	1964 30
1954 5,632	

According to published data, about 23 million tons of jet fuels were produced in 1960 in the USA; of these, 5 million tons were for commercial jet aviation. By 1964, the production of jet fuels is to be increased to 25-30 million tons, including about 10 million tons for commercial aviation.

Various types of fuels may be used in aviation gas-turbine engines — ranging from the lower grades of gasoline (mixed with other distillates) to kerosenes, even kerosenes including part of the fractions boiling just above 300°.

Apart from that of availability in large quantities, jet-aviation fuels are subject to a number of other specifications touching upon their operational characteristics as regards calorific value, low-temperature and anticorrosion properties, stability, and so forth.

Specifications for four types of jet fuels — T-1, TS-1, T-2 and T-5 — have been published in the Soviet Union; these are distinguished by the following requirements.

The T-1 and TS-1 fuels represent ligroin-kerosene fractions obtained by direct distillation of petroleum. T-1 fuel differs from TS-1 fuel in having a higher density, a heavier fractional composition, higher viscosity, and lower sulfur content.

T-1 and TS-1 fuels are products of direct distillation of petroleum; hence, they are stable and can be stored under warehouse condi-
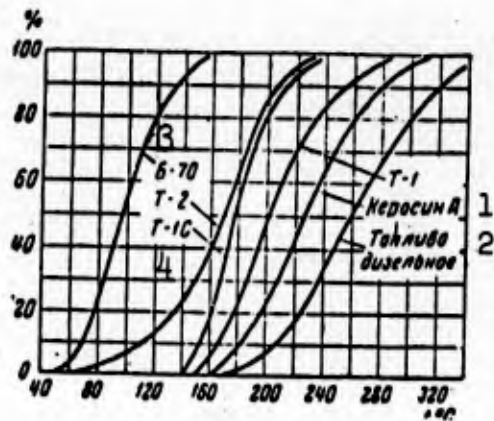
Fig. 31. Fractional composi-
tions of various fuels. 1)
Kerosene A; 2) Diesel fuel; 3)
B-70; 4) T-1S.
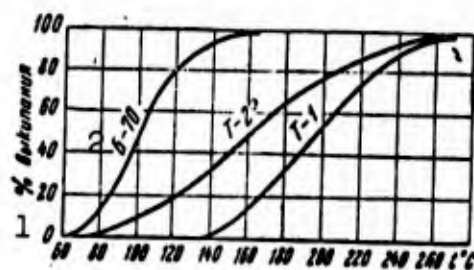
Fig. 32. Distillation curves
of aviation fuels. 1) Percent-
age distilled; 2) B-70.

tions for several years. Table 3 presents the technical specifications

for these fuels [5]. The thermal stability of T-5 fuel is determined

in the LSA-1 apparatus in 1 hour at 150°, in milligrams of sediment

per 100 ml of fuel or in a bomb during a 4-hour test at 150°.

The fractional compositions of the fuels are given in Figs. 31

and 32.

The actual compositions of the jet fuels are listed in Table 4

[6], which is based on analysis of a whole series of industrial con-

signments.

Unlike the direct-distillation jet fuels, fuel T-4 contains crack-

ing products and is therefore less stable.

In practical application of jet fuels in aviation and rocket en-

TABLE 3

Technical Specifications for T-1, TS-1, T-2, T-4 and T-5 Jet Fuels [5]

Показатели	Т-1 (ГОСТ 4138—49)	ТС-1 (ГОСТ 7149—54)	Т-2* (ГОСТ 8410—57)	Т-4* (ТУ 526—55)	Т-5 (ГОСТ 9145—59)
Плотность ρ_4^{20}	0,800—0,850	Не менее 0,775	Не менее 0,775	Не менее 0,755	Не менее 0,845
Фракционный состав:					
температура начала перегонки, не выше	150°	150°	Не ниже 60°	Не ниже 55°	105°
10% перегоняется при температуре, не выше . . .	175°	165°	145°	125°	225°
50% перегоняется при температуре, не выше . . .	225°	195°	195°	195°	—
90% перегоняется при температуре, не выше . . .	270°	230°	250°	250°	—
98% перегоняется при температуре, не выше . . .	280°	250°	280°	280°	315°
остаток и потери (%), не более	2	2	2	2	2
Вязкость кинематическая, сст:					
при 20°, не менее	1,5	1,25	1,05	1,0	Не более 5,0
» 0°, не более . .	4	2,5	—	3,0	—
»—40° » »	16	8,0	6,0	6,0	60
»—50° » »	25	—	—	—	—
Кислотность (мг КОН на 100 мл топлива), не более	1,0	1,0	1,0	1,0	1,0
Температура вспышки (определяется в закрытом тигле), не ниже	30°	28°	—	—	—
Температура начала кристаллизации (°C), не выше . . .	—60	—60	—60	—60	—60
Температура помутнения (°C), не выше . .	—50	—50	—	—50	—
Иодное число (г иода на 100 г топлива), не более . .	2	3,5	3,5	30	3,0
Содержание ароматических углеводородов (%), не более	25	22	22	30	22
Содержание фактических смол (мг на 100 мл топлива), не более:					
на месте производства. . .	8	7	7	15	8
на месте потребления. . .	11	10	10	—	11
Общее содержание серы (%), не более	0,1	0,25	0,25	0,4	0,1
в том числе меркаптановой, не более	—	0,01	0,01		—
Содержание водорастворимых кислот и щелочей . .	Отсутствуют			Отсутствуют	
Теплота сгорания низшая (ккал/кг), не менее	10250	10250	10250	10250	10250
Зольность (%), не более . . .	0,005	0,005	0,005	0,005	0,005
Содержание механических примесей и воды	Отсутствуют			Отсутствуют	
Испытание на медной пластинке	Выдерживают			Выдерживают	

*Saturation vapor pressure of T-2 fuel at 38° not above 100 mm Hg; for T-4, not above 150 mm Hg.

1) Index; 2) T-1 (GOST 4138-49); 3) TS-1 (GOST 7149-54); 4) T-2* (GOST 8410-57); 5) T-4* (TU 426-55); 6) T-5 (GOST 9145-59); 7) density ρ_4^{20}; 8) fractional composition: initial distillation temperature, not above; 9) 10% distilled at temperature not above; 10) 50% distilled at temperature not above; 11) 90% distilled at temperature not above; 12) 98% distilled at temperature not above; 13) residue and losses (%), not above; 14) kinematic viscosity, centistokes; 15) at 20°, not below; 16) acid number (mg of KOH per 100 ml of fuel), not above; 17) flash point (determined in sealed crucible), not below; 18) initial temperature of crystallization (°C), not above; 19) clouding temperature (°C), not above; 20) iodine number (g of iodine per 100 g of fuel), not above; 21) content of aromatic hydrocarbons (%), not above; 22) actual resin content (mg per 100 ml of fuel); 23) not above; 24) at point of production; 25) at point of use; 26) total sulfur content (%), not above; 27) including mercaptan sulfur content, not above; 28) content of water-soluble acids and alkalis; 29) lower-limit heat of combustion (kcal/kg), no less than; 30) ash content (%), not above; 31) mechanical-impurity and water content; 32) copper-plate test; 33) no less than; 34) not below; 35) no more than; 36) none; 37) passed.

TABLE 4

Factual Compositions of Jet Fuels

1 Показатели	2 T-1 (ГОСТ 4138—49)	3 TC-1 (ГОСТ 7149—54)	4 T-2 (ГОСТ 8410—57)	5 T-4 (ТУ 426—55)
Плотность ρ_4^{20}	0,800—0,823	0,773—0,780	0,758—0,770	0,769—0,784
Фракционный состав:				
температура начала перегонки	122—141°	122—140°	58—74°	78—95°
10% перегоняется при температуре	155—162°	141—153°	116—123°	120—131°
50% перегоняется при температуре	187—201°	164—177°	169—174°	162—173°
90% перегоняется при температуре	228—250°	205—220°	212—220°	218—228°
98% перегоняется при температуре	257—280°	223—240°	230—254°	233—253°
остаток и потери, %	1,5—2,0	1,5—2,0	1,5—2,0	1,5—2,0
Вязкость кинематическая, сст:				
при 20°	1,70—1,91	1,15—1,50	1,05—1,40	1,06—1,28
» 0°	2,67—2,94	1,79—1,94	1,40—1,57	1,26—1,84
» —40°	5,0—16,3	4,63—5,06	3,12—3,98	3,06—4,39
Кислотность, мг КОН на 100 мл топлива	0,19—0,57	0,06—0,29	0,07—0,40	0,3—0,9
Температура вспышки, определяемая в закрытом тигле	29—30°	27—33°	от —16° до —26°	от —12° до +1°
Температура начала кристаллизации	—60° и ниже	—60° и ниже	—57° и ниже	—55° и ниже
Температура помутнения	—45 и ниже —50°	—	—	—
Иодное число, г иода на 100 г топлива	0,5—2,40	0,87—2,6	0,17—3,6	1,8—15
Содержание фактических смол, мг на 100 мл топлива:				
на месте производства	—	—	—	—
на месте потребления	0,8—7,8	Следы + 8,8	Следы + 2,4	Следы + 4,0
Содержание ароматических углеводородов, %	10—25	13,8—19,4	12,0—23,4	19,6—27,8
Общее содержание серы, %	0,02—0,09	0,09—0,14	0,05—0,19	0,04—0,30
в том числе меркаптановой серы	Следы + +0,006	0,005—0,014	0,001—0,01	0,004—0,013
Испытание на медной пластинке	Выдерживают		Выдерживают	
Теплота сгорания низшая, ккал/кг	10 250— 10 315	10 350— 10 300	10 290— 10 380	10 275— 10 370
Зольность, %	0—0,0004	0+ следы	0—0,0014	0—0,002
Упругость насыщенных паров при 38°, мм рт. ст.	30—40	35—38	80—190	80—175

1) Index; 2) T-1 (GOST 4138-49); 3) TS-1 (GOST 7149-54); 4) T-2 (GOST 8410-57); 5) T-4 (TU 426-55); 6) density ρ_4^{20}; 7) fractional composition; 8) initial temperature of distillation; 9) 10% distilled at temperature of; 10) 50% distilled at temperature of; 11) 90% distilled at temperature of; 12) 98% distilled at temperature of; 13) residue and losses, %; 14) kinematic viscosity, centistokes; 15) at 20°; 16) acid number, mg of KOH per 100 ml of fuel; 17) flash point determined in sealed crucible; 18) initial temperature of crystallization; 19) clouding temperature; 20) iodine number, g of iodine per 100 g of fuel; 21)

factual resin content, mg per 100 ml of fuel; 22) at point of production; 23) at point of use; 24) aromatic-hydrocarbon content, %; 25) total sulfur content, %; 26) including mercaptan sulfur content; 27) copper-plate test; 28) lower-limit heat of combustion, kcal/kg; 29) ash content, %; 30) saturation vapor pressure at 38°, mm Hg; 31) and below; 32) traces to; 33) passed; 34) 0 to traces.

TABLE 5

Density Variation of Jet Fuels in Temperature Range from −40 to +200° [5]

1 Температура, °C	2 Плотность			
	T-1	3 TC-1	T-2	T-4
−40	0,8636	0,8240	0,8128	0,8150
−20	0,8496	0,8100	0,7988	0,8010
0	0,8335	0,7947	0,7832	0,7871
+20	0,8210	0,7796	0,7663	0,7721
+40	0,8074	0,7650	0,7512	0,7584
+60	0,7921	0,7498	0,7363	0,7444
+80	0,7778	0,7342	0,7223	0,7304
+100	0,7636	0,7212	0,7083	0,7164
+120	0,7496	0,7072	0,6943	0,7024
+150	0,7286	0,6832	0,6733	0,6814
+175	0,7111	0,6657	0,6558	0,6639
+200	0,6936	0,6482	0,6383	0,6464

1) Temperature, °C; 2) density; 3) TS-1.

TABLE 6

Viscosity Variation of Jet Fuels in Temperature Range from −50 to +150°

1 Температура, °C	2 Вязкость, ccm			
	T-1	3 TC-1	T-2	T-4
−50	14,93	7,92	4,76	5,11
−40	8,50	5,15	4,41	3,76
−20	4,13	2,82	2,13	2,14
0	2,47	1,82	1,47	1,53
+20	1,63	1,27	1,13	1,08
+40	1,21	0,90	0,89	0,96
+60	0,92	0,81	0,73	0,81
+80	0,75	0,69	—	—
+100	0,64	0,56	—	—
+120	0,54	0,49	—	—
+140	0,46	0,43	—	—
+150	0,45	0,42	—	—

1) Temperature, °C; 2) viscosity, centistokes; 3) TS-1.

gines, a factor of great importance is the variation in the fuel's properties over a wide temperature range; this may be associated with the use of the fuels under summer or winter conditions, or with heating of the fuel in the engines under operational conditions.

Values indicating the density changes of the fuels in the temperature range from −40 to +200° are listed in Table 5.

The viscosity changes of jet fuels in the temperature range from −50 to +150° are listed in Table 6.

The ranges of variation of the elementary fuel compositions are presented below:

Fuel	Content, %	
	C	H
T-1	86,02—86,04	13,38—13,68
T-2	85,5—85,72	14,22—14,34
TC-1	85,75	14,05
T-4	85,34—85,88	14,09—14,33

The moisture content of the fuels listed above lies between 0.012 and 0.005%.

The contents by weight of nitrogen, oxygen and sulfur compounds in TS-1 fuel are of the following order (in %):

        Sulfur compounds.................... 1.13
        Oxygen compounds.................... 0.17
        Nitrogen compounds................. 0.03

These data were computed from an actual sulfur content of 0.25%, the content of the other (O and N) compounds, and an average molecular weight of 148.

Several specifications for jet fuels have appeared in the USA in recent years [2-7]; see Tables 7 and 8.

JP-1 fuel (which also carries the codes MIL-F-5616 and AN-F-32) is a narrow kerosene fraction. According to certain as yet inadequately confirmed reports, JP-1 fuel is no longer used in the Air Force, but may be regarded as a high-quality fuel for commercial jet aircraft.

TABLE 7

Technical Specifications for Turbojet Fuels used
Abroad (USA, England, France)

1 Показатели	JP-1	JP-2	JP-3	DERD-2482	CP-811	JP-4	JP-6
2 Содержание ароматических углеводородов (объемн. %), не более	20	20	25	20	20	20	25
3 Бромное число не более	3,0	3,0	30,0	—	—	—	0
4 Сера (вес. %), не более	0,20	0,20	0,50	0,20	0,1	0,4	0,4
5 Плотность при 15,5°, не более	0,85	0,85	0,725—0,801	Не ограничивается 20	0,82	0,746—0,825	0,70—0,83
6 Температура замерзания (°C), не выше	—60	—60	—60	—40	—	—60	—40
7 Содержание меркаптановой серы (%), не более	—	—	0,005	—	—	0,005	—
8 Температура вспышки (°C), не ниже	43	—	—	38	43	—	38
9 Упругость пара при 38°, $кг/см^2$ (мм рт. ст.)	—	0,14—0,21	0,35—0,49	—	—	130—160	55
10 Фракционный состав:							
11 начало кипения	—	65,5°	70°	—	—	65°	210°
12 10% выкипает до	210°	—	—	—	210°	121°	—
20 » »	—	—	—	200°	—	—	—
30 » »	254°	—	204°	—	254°	—	—
13 конец кипения	300°	260°	315°	300°	—	288°	295°
14 Остаток при испарении в воздушной струе, мг/100 мл	5,0	5,0	10,0	6,0	—	—	—
15 Смолы (мг/100 мл) не более	8,0	8,0	20,0	—	—	—	—
16 Коррозия	Нет	Нет	Нет 21	—	—	—	—
17 Вязкость при —40°, сст	10	10	10	6,0	10	—	10
18 Теплотворная способность (ккал/кг) не менее	10 170	10 220	10 212	10 156	—	10 220	10 160
19 Содержание антиокислителя, мг/л	—	—	24	—	—	24	—

1) Index; 2) aromatic-hydrocarbon content (% by volume), not above; 3) bromine number, not above; 4) sulfur (% by weight), not above; 5) density at 15.5°, not above; 6) solidification point ($^\circ$C), not above; 7) content of mercaptan sulfur (%), not above; 8) flash point ($^\circ$C), not below; 9) vapor pressure at 38°, kgf/cm^2 (mm Hg); 10) fractional composition; 11) initial boiling; 12) 10% distilled below; 13) end of boiling; 14) residue on evaporation in air jet, mg/100 ml; 15) resins (mg/100 ml), not above; 16) corrosion; 17) viscosity at -40°, centistokes; 18) calorific value (kcal/kg), not less than; 19) antioxidant content, mg/liter; 20) not restricted; 21) none.

According to the same sources, JP-2 fuel (AN-F-34) was only an experimental fuel and was not accepted for further use. JP-3 fuel (MIL-F-5624 and AN-F-58), which has a broadened fractional composition with a vapor

Actual Characteristics of VRD* Fuels [7-8]

1 Показатель	JP-1	JP-2	JP-3	JP-4	JP-5
2 Плотность при 15,5°	0,814	0,704	0,702	0,764	0,83
3 Упругость паров при 38°, мм рт. ст.	—	315	368	134—160	55
4 Фракционный состав:					
5 10% выкипает до	174°	—73°	66°	84—102°	185°
50	192°	156°	173°	142—147°	—
90	225°	224°	240°	209—227°	273° (к. к.) [17]
6 Теплотворная способность, ккал/кг	10 300	10 300	10 270	10 400	10 370
7 Остаток при испарении в воздушной струе при 204°, мг на 100 мл топлива	1,4	1,7	1,2	1,7	—
8 Содержание серы, %	0,079	0,085	0,35	0,074—0,119	0,20
9 Содержание меркаптановой серы, %	0,0009	0,0008	0,005	0,0017	—
10 Бромное число	0,95	2,59	7,3	1,4	—
11 Температура вспышки, °C	48	—	—23	—13,8	38
12 Вязкость при —40°, сст	2,29	2,91	3,36	2,51	6 (при 0°) [18]
13 Анилиновая точка, °C	56	57	41	58	—
14 Содержание ароматических углеводородов, объемн. %	14,3	11,3	25	10—12	20
15 Температура замерзания, °C	—60	—60	—60	—60	—40
16 Растворимость воздуха в топливе, объемн. %	—	—	—	—	14

[*Air-Breathing Reaction-Thrust-Engine.]
1) Index; 2) density at 15.5°; 3) vapor pressure
at 38°, mm Hg; 4) fractional composition; 5) 10%
distills below; 6) calorific value, kcal/kg; 7)
residue from evaporation in air jet at 204°, mg
per 100 ml of fuel; 8) sulfur content, %; 9) mer-
captan-sulfur content, %; 10) bromine number; 11)
flash point, °C; 12) viscosity at —40°, centi-
stokes; 13) aniline point, °C; 14) aromatic-hydro-
carbon content, % by volume; 15) solidification
point, °C; 16) solubility of air in fuel, % by
volume; 17) [end of boiling]; 18) at 0°.

pressure of 267-374 mm Hg is in extensive use, but the high vapor pres-
sure makes use of this fuel difficult at the low pressures prevailing
at high altitudes. JP-4 fuel, which has a vapor pressure of 107-160
mm Hg is not host to this shortcoming. It is based on direct-distilla-
tion products and products of thermal and catalytic cracking. JP-5
fuel (MIL-F-5624B) is produced on the same basis. It can also be pro-

duced by hydrolytic cracking. The initial temperature of crystallization for JP-5 fuel has been raised to -40°, and its fractional composition is heavier than the other fuels. JP-1, JP-4 and JP-5 fuels are less of a fire hazard than JP-2 and JP-3 fuels and aviation gasoline.

MIL-F-5572 or AN-F-48 aviation gasolines are used as starting fuels.

Let us examine the specifications for fuels for air-breathing reaction engines (Table 7) and the actual operational characteristics of these fuels (Table 8) [2-7].

Fuels of broad fractional composition may be used for aircraft equipped with turboprop engines.

JP-4 fuel is recommended for supersonic aviation at flight speeds up to 1800 km/hr; as a heavier fuel, JP-5 is recommended for velocities up to 3600 km/hr; here, part of the fuel may be fed to the engine in vaporized form due to the appreciable heating of the aircraft and its tanks from friction with the air.

Other aviation fuels have been reported [8a]. JP-6 fuel has a boiling range from 120 to 290°, a density of 0.78 to 0.84, a solidification point of -51°; RJ-1 fuel has a boiling range from 200 to 320°, a density of 0.84 to 0.86, a solidification point of -40° and a flash point of $+88^{\circ}$; RP-1 fuel boils in the range from 195 to 275°, and has a density of 0.80 to 0.82, a solidification point of -40°, and a flash point of $+43^{\circ}$.

JP-6, RJ-1 and RP-1 fuels are thermally stable kerosenes that have been specially purified. JP-6 is recommended for flight speeds from 1800 to 2400 km/hr, RJ-1 (heavy kerosene) for ramjet aircraft and speeds of 2400-3600 km/hr; RP-1 is a fuel with a low aromatic-hydrocarbon content and high completeness of combustion.

All new supersonic-aviation fuels are distinguished by higher

solidification points, heavier fractional compositions, and high chemical stability.

In 1959, 322 thousand tons of fuels were used for supersonic aviation in the USA; this corresponds to 2.3% of the annual jet-fuel consumption.

A characterization of supersonic aviation fuels is presented in Table 9.

TABLE 9
Characterization of Fuels for Supersonic Aviation
[9]

Топливо 1	Плотность при 15,5° 2	Пределы выкипания, °C 3	Температура вспышки, °C 4	Температура замерзания, °C 5	Низшая теплотворная способность, $Q_н$ 6	Вязкость, сст 7
JP-5	0,788—0,845	176—288	60	—48	10 168	16,5 (—34°)
JP-6	0,78—0,84	121—288	—	—53		
JP-X	0,876—0,976	230—283	—	—60		
RS-1	0,842—0,863	204—315	88	—40		
RS-1*	0,802—0,876	193—274	43	—40		1,25—3,18

*Purified highly stable direct-distilled kerosene,
Q_N = 10,312 kcal/kg.
1) Fuel; 2) density at 15.5°; 3) boiling range, ^{O}C;
4) flash point, ^{O}C; 5) solidification point, ^{O}C;
6) lower-limit calorific value, Q_N; 7) viscosity,
centistokes.

The fractional compositions of the fuels are presented in Fig. 33. When cracking products are used, the yield of broad-fraction jet fuel may reach 50-55% of the petroleum processed (Fig. 34).

On the other hand, the yield of jet fuel from petroleum is limited by the solidification point and the admissible boiling range. The higher the solidification temperature tolerated, the higher the terminal boiling point of the fuel that can be used and, consequently, the higher the yield.

This is illustrated by the data of Table 10, which apply to petro-
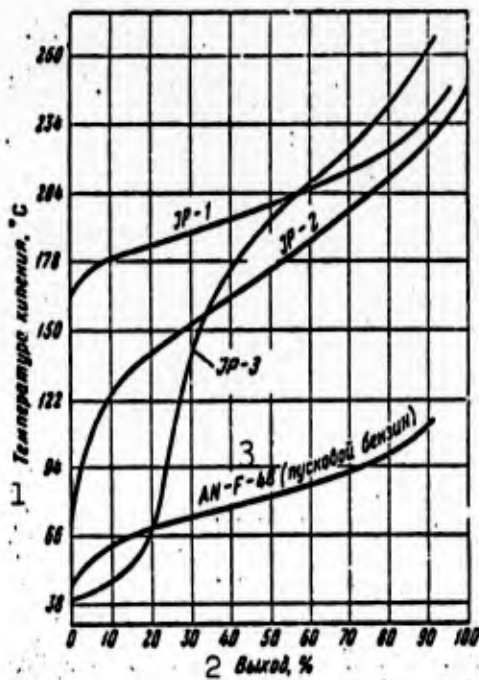
Fig. 33. Fractional composition of certain jet fuels. 1) Boiling point, ^{o}C; 2) yield, %; 3) AN-F-48 (starting gasoline).
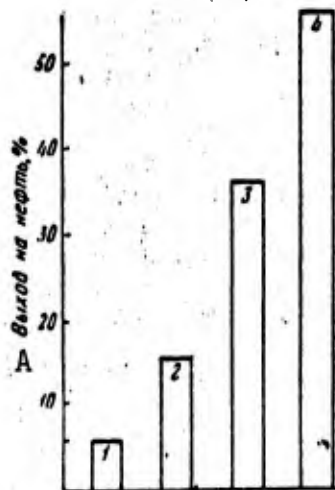
Fig. 34. Average yield of jet fuels from petroleum as a function of fractional composition of fuel. 1) JP-1 fuel; 2) JP-2 fuel; 3) JP-3 fuel produced by direct distillation; 4) JP-3 fuel produced by direct distillation and cracking. A) Yield referred to petroleum, %.

TABLE 10

Solidification Point and Yield
of Jet Fuel from Middle Eastern
Petroleums

1 Топливо	Температура замерзания, °C 2	Выход на нефть, вес.% 3
4 Топливо типа керосина	—40	25
5 То же	—60	10
6 Топливо широкого фракционного состава	{ —40 —60	50 35

1) Fuel; 2) solidification point,
°C; 3) yield on petroleum, % by
weight; 4) kerosene-type fuel;
5) same; 6) fuel with broad frac-
tional composition.

leums from the Middle East.

The majority of jet fuels for aviation are subject to the require-
ment that the solidification point be no higher than —60°. However,
experience in the use of the fuels indicates that at an altitude of 10
to 12 km, where the ambient temperature is about —55°, the temperature
of the fuel in the tanks and pipelines does not drop below —30° in
flight at 600-770 km/hr.

2. Hydrocarbon Combustibles for Rocket Engines

After the Second World War, as a result of extensive research,
hydrocarbon combustibles were placed at the disposal of rocket engi-
neering. Prior to 1950, alcohols were used as fuels for oxygen-based
propellants and amines as fuels for nitric-acid propellants.

Thus, in 1952, the USA's "Nike" antiaircraft rocket used as the
fuel for its nitric-acid propellant JP-3 broad-fraction aviation kero-
sene, which was subsequently replaced by JP-4 aviation kerosene.

In the USA's intermediate-range ballistic missile "Thor" and the
intercontinental "Atlas" missile (USA), RP-1 rocket kerosene is used
as the fuel in combination with oxygen [10, 11].

Subsequently, a fuel based on pyrolysis products and known as "HF-D" was proposed in the USA for engines operating on nitric acid with nitrogen oxides. It has the following composition:

Initial boiling temperature........ 122°
Temperature at 50% distilled....... 165°
End of boiling..................... 220°
Density............................ 0.94
Solidification point............... -73°
Viscosity at 21°.................. 1.714 cst

This fuel possesses a higher chemical activity with respect to nitric acid than do the JP-3 and JP-4 kerosenes.

A fuel produced from coal-tar resin and containing dibasic phenols has high chemical activity.

RP-1 kerosene, which is widely used in American liquid-engine rockets as a fuel paired with oxygen, is a special kerosene with an elevated content of cyclic hydrocarbons and a reduced content of paraffinic hydrocarbons. Research has shown that cyclic hydrocarbons possess higher thermal stability and produce smaller amounts of deposits than do the paraffinic hydrocarbons when the fuel is used to cool the engine. When RP-1 kerosene was produced in small quantities, its properties were sufficiently stable from batch to batch, but when production was expanded, the physical and chemical properties of this fuel began to vary from batch to batch over a very wide range. RP-1's increased content of straight-chain hydrocarbons, which possess lower thermal stability than cyclic hydrocarbons, results in an increased tendency of RP-1 kerosene to undergo coking and, consequently, a deterioration in its cooling properties.

The specific gravity of RP-1 kerosene at 15° may vary in the range from 0.801 to 0.875, while it lies between 0.800 and 0.785 at 38°; the maximum viscosity at 38° is 3.185 centistokes, while the min-

TABLE 11

Average Values of Isothermal-Compressibility Coefficient of RP-1 Kerosene at Pressures below 500 kgf/cm^2

1) Коэффициент изотермической сжимаемости, $\beta \cdot 10^6$ атм$^{-1}$					
0°	30°	75°	150°	245°	300°
33	60,8	74,8	110,8	167,5	264
54,2	61,6	76,5	114	173,5	276
54,8	62,9	77,9	117	178	287
55,2	63,4	79,5	120	184	208
55,6	64,5	81	123	189,5	310

1) Isothermal-compressibility coefficient, $\beta \cdot 10^6$ atm^{-1}.

imum is 1.250 centistokes.

In addition to their general physicochemical properties, such properties as compressibility are of great importance for rocket kerosenes. The compressibility and thermal expansion of kerosene specimens from different petroleums differ by more than 30% at high temperatures for a given molecular weight.

RP-1 kerosene is used in the engine as a coolant in cases of regenerative cooling. It is heated on passage through the engine jacket, but its maximum temperature never exceeds 300°.

The isothermal-compressibility coefficient of RP-1 kerosene is given in Table 11.

The wide variation of the density of RP-1 kerosene complicates the process of fueling the rockets, regulating the engines, and so forth.

As a result, research was carried out to find synthetic fuels that would have characteristics more stable than those of RP-1 kerosene, but properties closely similar to those of RP-1.

The investigations carried out indicated that the following cyclic hydrocarbons may be used as substitutes for RP-1 kerosene:

TABLE 12

Properties of Certain Naphthenes

1 Углеводород	Плотность, ρ_4^{20} 2	Т. кип., °C 3	Теплота сгорания, ккал/моль 4	Формула 5
6 1,2-Диэтилциклогексан	—	176,1	—	C_2H_5 CH H_2C CH—C_2H_5 H_2C CH$_2$ CH$_2$
7 1,3-Диэтилциклогексан	0,7986	173,5	1511	C_2H_5 CH H_2C CH$_2$ H_2C CH—C_2H_5 CH$_2$
8 1,4-Диэтилциклогексан	0,806	174,6	1511	C_2H_5 CH H_2C CH$_2$ H_2C CH$_2$ CH C_2H_5
9 Декалин (транс)	0,872	185	1497,1	CH$_2$ CH$_2$ H_2C CH CH$_2$ H_2C CH CH$_2$ CH$_2$ CH$_2$

1) Hydrocarbon; 2) density ρ_4^{20}; 3) boiling point, °C; 4) heat of combustion, kcal/mole; 5) formula; 6) 1,2-diethylcyclohexane; 7) 1,3-diethylcyclo-hexane; 8) 1,4-diethylcyclohexane; 9) decalin (<u>trans</u>).

decalin   diethylcyclohexanes
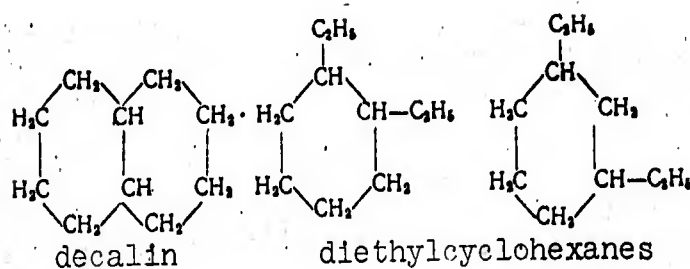
Diethylcyclohexane, which is the cheapest and simplest to produce, shows great promise. At the present time, the rate of its production in the USA is two to three times the quantity necessary to service the development program for long-range ballistic rockets.

The production of diethylcyclohexane may be set up on the basis of styrene production.

An intermediate product in the production of styrene is ethylbenzene, which is obtained by alkylation of benzene with ethylene. Together with the ethylbenzene, 10 to 15% of diethylbenzene is produced as a byproduct:

$$C_6H_6 + C_2H_4 \left\langle \begin{array}{l} C_6H_5 - C_2H_5 \\ C_6H_4(C_2H_5)_2 \end{array} \right.$$
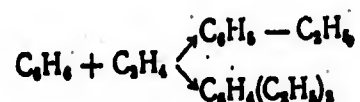
Subsequently, the ethylbenzene is converted into styrene by dehydration of the side chain.

In view of the fact that styrene production in the USA in 1960 was over 600,000 tons, 60,000 to 90,000 tons of the diethylbenzene byproduct may be produced.

Diethylcyclohexane is produced by hydration of diethylbenzene.

Diethylcyclohexane is a colorless liquid having the empirical formula $C_{10}H_{20}$. The molecular weight of diethylcyclohexane is 140, its density corresponds to that of RP-1 kerosene (0.80 to 0.81), its heat of combustion is 10,328 kcal/kg and somewhat higher than that of RP-1 kerosene; its solidification temperature is below -80°, its flash point is $+47^\circ$; diethylcyclohexane cokes to a lesser degree than does RP-1 kerosene (Table 12).

A mixture of polycyclic naphthenes produced by hydrogenation of aromatic hydrocarbons is also recommended for rocket engines. The polycyclic naphthenes have the following properties:

Specific gravity.................... 0.87-0.89°

Boiling-temperature range.......... 201-275°
Solidification point............... -60°
Calorific value.................... 10,200 kcal/kg

3. Pumpability of Fuels

The solidification and clouding temperatures of fuels determine the possibility of using them at high altitudes. Solidification of fuel begins with precipitation of crystals of the hydrocarbons having the highest melting points, as well as precipitation of ice on freezing of the dissolved water. The rest of the hydrocarbons solidify as the temperature is depressed still further. The crystals that have formed clog the fuel filters, so that fuel feed may be reduced or may cease altogether even before the basic mass of the fuel has frozen [10].

Irrespective of the time of year, the ambient temperature at altitudes above 10 km reaches -55°. However, it must be remembered that at high flight speeds of the aircraft (of the order of 950-1000 km/hr), air friction raises the skin temperature and the temperature inside the aircraft by no less than 30-35°. At speeds of the order of 1300 km/hr, this increase rises as high as 60° above the ambient-air temperature (-55°). In this connection, certain foreign specialists have expressed the opinion that the solidification temperature of fuels may be raised henceforth to -45°. In this case, the yield of jet fuel from the petroleum could be increased considerably. As the flight speed is further increased to 2000-2500 km/hr, heating of the aircraft becomes such a problem that it must be countered by means of special measures, including the use of special cooling techniques and heavy fuels with very low vapor pressures.

High vapor pressure in a fuel influences its delivery from the tanks to the engine when pump sets are used, since vapor locks may form at depressed pressures, and this interferes with fuel feed. The

tendency of the fuel to form vapor locks may be characterized by the
ratio of vapor- to liquid-phase volumes at a specified pressure: v/L.

Figure 35 shows the ratio of $\underline{v}$ to L as a function of flight alti-
tude for fuels of the aviation-kerosene and aviation-gasoline types.
For a given pump-feed system, the critical ratio v/L is 2. At this
point, vapor locks form in the fuel-feed system and normal operation
of the system is disturbed. For gasoline, this ratio is reached at an
altitude of 4570 m and for kerosene at an altitude of 16,750 m at a
fuel temperature of $+38^\circ$ [10].

In the wide-fraction fuels JP-2 and JP-4 (initial boiling 60° and
terminal boiling 280°), reliable operation of the fuel-feed system is
ensured up to an altitude of 10-12 km.
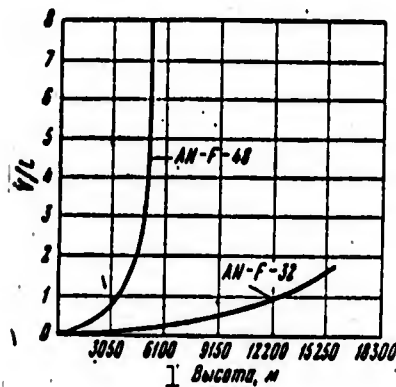
Fig. 35. Ratio of volumes of
vapor and liquid phases for
fuels of gasoline and kerosene
types. 1) Altitude, meters.

Figure 36 shows the variation of pump-set output for kerosene-
and gasoline-type fuels as a function of the external pressure. Secur-
ing a gasoline-feed rate to the engine equal to that of kerosene re-
quires pumps 2 to 4 times larger than those used for kerosene.

The viscosity of the fuel influences its pumpability and particu-
larly the proficiency with which it is atomized. This factor deter-
mines the droplet size, outflow speed, and spray-cone angle of the

- 96 -
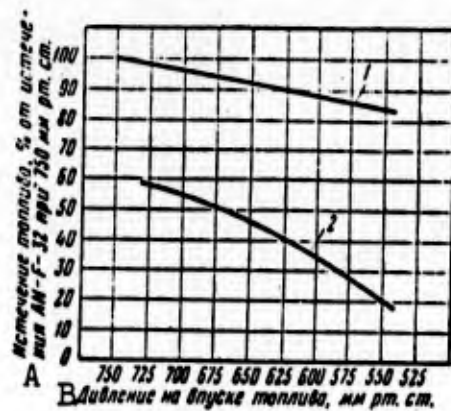
Fig. 36. Variation of fuel-
pump output as a function of
fuel type and ambient pressure.
1) AN-F-32; 2) AN-F-48 (vapor
pressure after Reyd [sic] 0.49
kgf/cm^2). A) Fuel outflow in %
of outflow of AN-F-32 at 750
mm Hg; B) fuel intake pressure,
mm Hg.
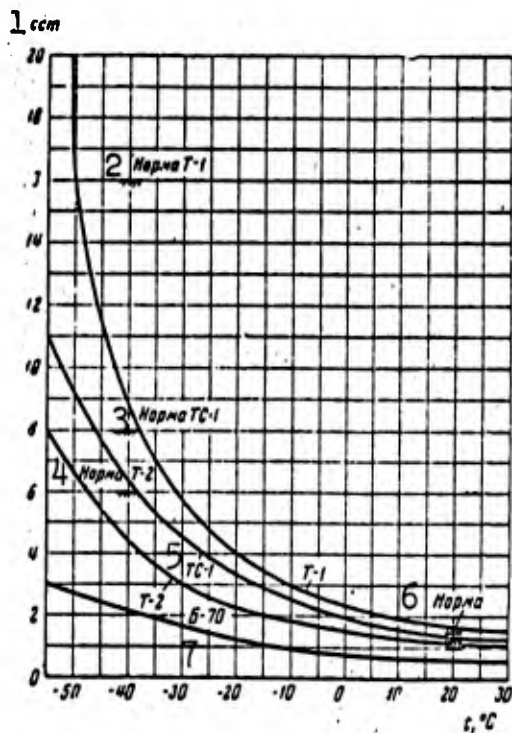
Fig. 37. Viscosity of jet fuels
as a function of temperature.
1) Centistokes; 2) T-1 stand-
ard; 3) TS-1 standard; 4) T-2
standard; 5) TS-1; 6) standard;
7) B-70.

fuel. The variation of the viscosity of various jet fuels as a func-
tion of temperature is shown in Fig. 37.

- 97 -
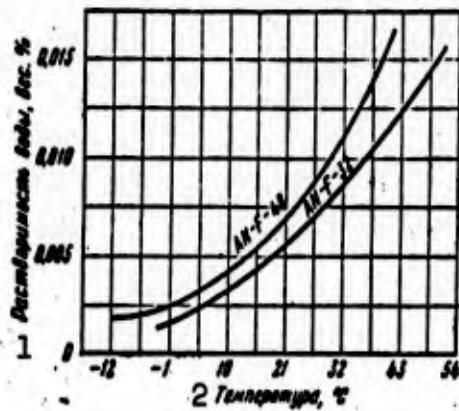
Fig. 38. Solubility of water
in aviation fuels at various
temperatures. 1) Solubility of
water, % by weight; 2) tem-
perature, °C.
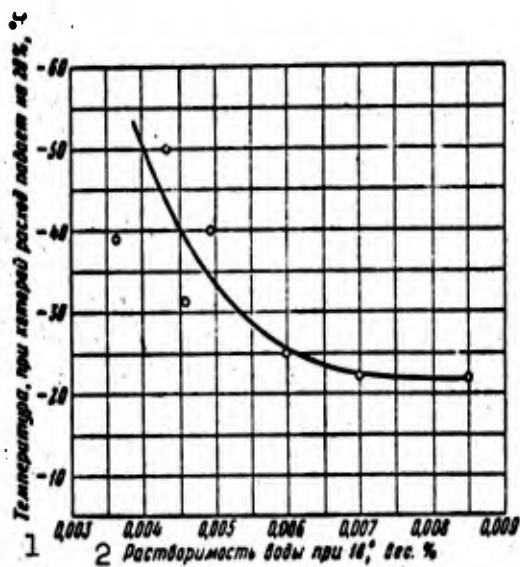
Fig. 39. Solubility of water
in fuel and its influence on
ice clogging of filters. 1)
Temperature at which flow rate
drops by 20%, °C; 2) solubility
of water at 18°, % by weight.

The most important factor exerting a detrimental influence on

fuel feed is clogging of the fuel filters by ice crystals as a result

of freezing of water at low temperatures. Under normal conditions, the

hydrocarbons forming the fuel have dissolved in them a certain quan-

tity of water (about 0.005%). At low temperatures, the solubility of

the water is lowered and the separated water precipitates in the form

- 98 -

of fine crystals.

Figures 38 and 39 show the solubility of water in hydrocarbons and in fuels of the kerosene and gasoline types. Even at -15°, the major part of the water has precipitated from the kerosene in the form of ice. Solid paraffins are precipitated simultaneously with the ice crystals. They may cause partial or complete clogging of the filter.

When kerosene containing 0.005% of water is cooled to -16°, about 0.004% of water may be separated in the form of ice. With 4500 liters per hour of fuel flowing through the filter, as much as 0.18 kg of ice crystals may be accumulated on the filter during an hour. In the majority of cases, this ice is deposited to some extent on the walls of the tank. However, under conditions of rapid cooling, the ice may remain suspended and be carried by the fuel into the feed system, where it lodges on the filter.

The greater the quantity of water dissolved in the fuel, the greater the quantity that will be precipitated on cooling.

The solubility of water in a fuel depends on the latter's chemical composition.

Table 13 shows the solubility of water at 18° in a number of fuels.

The solubility of water in a fuel depends on the latter's aromatic-hydrocarbon content for a given fractional composition.

Below we list the solubilities of water in various hydrocarbons at $22-25^{\circ}$:

Temperature, $^{\circ}$C	Solubility, %
Normal pentane...25	0.011
Normal heptane...25	0.015
Benzene..........22	0.066
Toluene..........22	0.052
Xylene...........22	0.038

A certain relationship obtains between the solubility of water in

- 99 -

TABLE 13

Solubility of Water in Various Fuels

1 Топливо	Плотность при 15° 2	Пределы кипения, °C 3	Содержание ароматических углеводородов, % 4	Растворимость воды при 18°, % 5
6 Бензин	0,735	44—171	22,2	0,007
7 Керосин	0,825	184—297	4,4	0,003
	0,806	158—276	8,6	0,006
	0,834	143—262	21,9	0,008

1) Fuel; 2) density at 15°; 3) boiling-temperature range, ^oC; 4) aromatic-hydrocarbon content, %; 5) solubility of water at 18°, %; 6) gasoline; 7) kerosene.

a fuel and clogging of the filter. The higher the solubility of water in the fuel, the higher will be the temperature at which the tendency to ice-crystal clogging of the fuel filter appears.

There is also a certain relationship between the clouding temperature (the clouding temperature is usually several degrees higher than the solidification temperature) and the temperature at which the flow rate of the fuel is observed to have dropped by 20%. In jet fuels, the clouding temperature lies between -40 and -60°, but is not usually above -50°.

Low-temperature filter clogging is prevented by adding certain substances to the fuel that raise the solubility of water at low temperatures.

Thus, ice clogging of the filters is completely eliminated by adding to the fuel from 0.5 to 1% of isopropyl alcohol, which is quite soluble in hydrocarbons and dissolves water adequately. Obviously, many other substances with similar physicochemical nature can be used for this purpose.

Another factor that may influence the flow rate and atomization of the fuels is the variation of their density.

The densities of different specimens of turbojet fuels lie in the range from 0.76-0.82-0.85 at normal temperatures. At low temperatures, density increases, and this characteristic influences the flow of the fuel through the nozzles, since the pumps are adjusted to deliver a certain volume of fuel. The same applies to the outflow of the fuel through the nozzles.

Figure 40 shows the variation of the densities of jet fuels as functions of temperature.

The variation of fuel density as a function of temperature may be computed approximately by the formula

$$\gamma_t = \gamma_t^{20} \pm \gamma' \, (t - 20),$$

where γ is the density of the fuel at 20° and γ' is the coefficient of expansion; for fuels with specific gravities in the range from 0.80 to 0.82, $\gamma = 0.00075$.
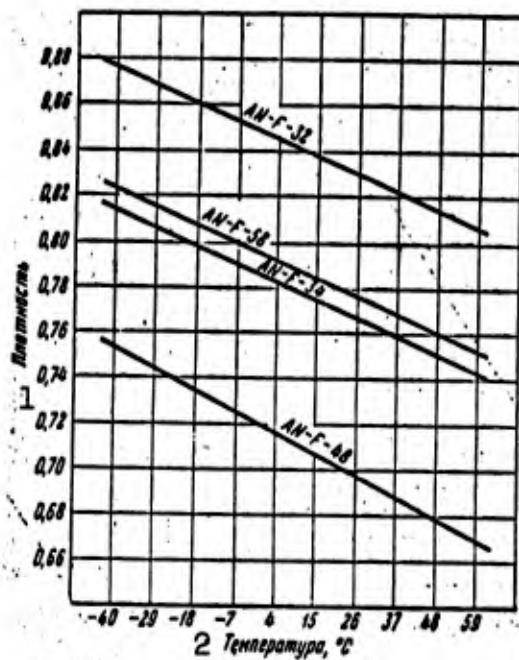
Fig. 40. Variation of jet-fuel densities as functions of temperature. 1) Density; 2) temperature, $^\circ$C.

At a temperature of -50°, the density of the fuel has increased

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TABLE 14

Mean Volumetric-Expansion Coeffi-
cients of Petroleum Products

Предел измене- ния плотности 1	Средний коэффициент расширения a 2	Предел измене- ния плотности 1	Средний коэффициент расширения a 2
0,76 —0,780	0,001054	0,880—0,900	0,000734
0,780—0,800	0,000995	0,900—0,920	0,000688
0,800—0,820	0,000937	0,920—0,940	0,000645
0,820—0,840	0,000882	0,940—0,960	0,000604
0,840—0,860	0,000831	0,960—0,980	0,000564
0,860—0,880	0,000782	0,980—1,000	0,000526

1) Range of density variation; 2)
mean expansion coefficient α.

to 0.87 from the original 0.82 at $+20^{\circ}$.

In supersonic flight, on the other hand, when the tanks may be
heated to +100 to 200°, we must reckon with volumetric thermal expan-
sion of the fuels. The volumetric-expansion coefficients of heavy
fuels are smaller than those of light fuels: for JP-1, we have $\sim10\cdot10^{-5}$,
while for JP-4, we have $94\cdot10^{-5}$.

Thus, a fuel with a specific gravity of 0.80 to 0.82 undergoes a
9.4-percent change in volume on heating to 100°, while a fuel with a
specific gravity of 0.96 to 0.98 changes volume by 5.6%.

The thermal expansion of a fuel is determined by the formula

$$v_t = v_0 \left(1 + a \cdot t\right),$$

where $\underline{v}$ is the volume at the subject temperature, v_0 is the volume at
the initial temperature, $\underline{t}$ is the temperature change, and α is the
volumetric expansion coefficient.

We tabulate the temperature coefficients of volumetric expansion
of petroleum products as functions of their specific gravity (Table 14).

4. Fuel Losses at High Altitude

An important problem encountered in using jet fuels is that of
countering fuel losses at high altitudes, both as a result of direct

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evaporation at the low pressures and as a result of bumping of the fuel on liberation of the dissolved air [7, 12].
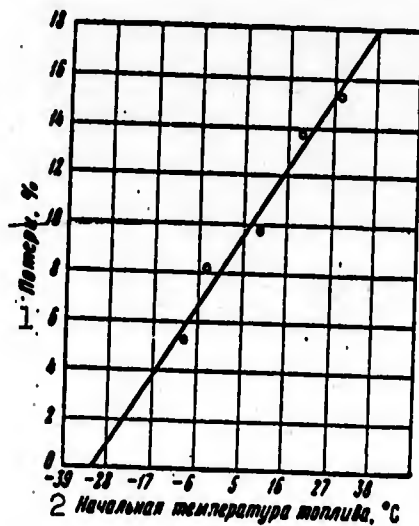
Fig. 41. Weight losses of fuel at high altitudes as functions of initial temperature of fuel at altitude of 18 km (rate of climb 300 m/sec). 1) Losses, %; 2) initial temperature of fuel, °C.
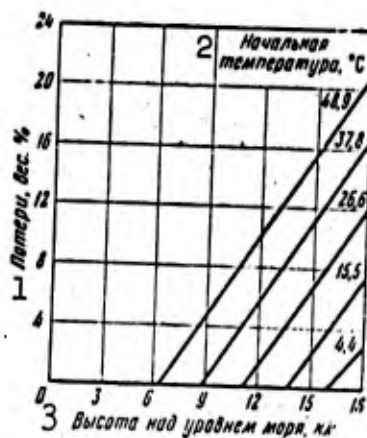
Fig. 42. Weight losses of fuel at various altitudes as functions of fuel temperature (rate of climb 300 m/sec). 1) Loss, % by weight; 2) initial temperature, °C; 3) altitude above sea level, km.

The solubility of air in petroleum products diminishes as their surface tension increases. Gasolines dissolve approximately 20 to 25%

TABLE 15

Solubility of Air in Various Petroleum Products

1 Нефтепродукт	Плотность при 21°	Поверхностное натяжение при 21°, дин/см	Растворимость, объемн. %
5 Авиационное топливо . .	0,780	23,45	17,2
» »	0,723	18,70	22
» »	0,690	17,70	25
6 Смазочное масло	0,882	29,30	7,25
» . . »	0,860	28	11,30

1) Petroleum product; 2) density at
21°; 3) surface tension at 21°,
dynes/cm; 4) solubility, % by volume;
5) aviation fuel; 6) lubricating oil.

TABLE 16

Comparison of Fuel Losses at Altitude of 18.3 km

1 Топливо	Давление пара при 37,8°, кг/см°	3 Потери (вес. %) при начальной температуре	
	2	15,5°	37,8°
4 Керосин	0,007	0,0	0,0
5 Топливо широкого фракционного состава . . .	0,136	0,0	1,0
6 То же	0,47	9,6	15,0

1) Fuel; 2) vapor pressure at 37.8^o,
kgf/cm^2; 3) losses (% by weight) at
initial temperature of; 4) kerosene;
5) broad-fraction fuel; 6) same.

by volume of air, kerosenes 13-15%, and lubricating oils 7-11%. The

solubility of air in paraffinic hydrocarbons is higher than in aromatic

hydrocarbons.

The solubility of air varies only slightly as a function of tem-

perature and to a considerably greater degree as a function of pres-

sure. At low pressures, therefore, the air begins to separate. The gas

separated from kerosene is richer in oxygen than air and contains about

32.6% of this element, while air contains about 21% of oxygen. This

raises the explosion hazard for the fuel in the tanks.

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The losses of fuel with the evolved air at low pressures are not, in themselves, large. Thus, they amount to 0.028-0.031% by weight at an altitude of 9150 meters for a 0.35-0.45-kgf/cm^2 vapor pressure over JP-3 fuel.

Although the fuel losses in the form of vapor with the evolved air are not in themselves large, they may be increased as a result of bumping of the fuel and ejection of the fuel through the air lines.

The solubilities of air in various petroleum products are given in Table 15.

The fuel losses at high altitudes depend on the initial temperature of the fuel. Figure 41 shows the losses of a gasoline-type fuel with a density of 0.74, an initial-boiling temperature of 30°, and a final-boiling temperature of 204° at an altitude of 18.3 km as a function of the fuel's initial temperature, for a 300-m/sec rate of climb.

At a temperature of 27°, the fuel losses amount to 15%, but on cooling to −17°, the fuel loses no more than 4%.

Figure 42 presents the weight losses of fuels at various altitudes and at various fuel temperatures.

Table 16 gives the losses of various fuels at an altitude of 18.3 km as functions of the vapor pressure and initial temperature.

Thus, the fuel losses may be quite considerable for high rates of climb.

Fuel losses may be reduced by using hermetically sealed tanks and freezing the fuel on the ground. The use of the first method involves increasing the weight of the aircraft, while the second requires expensive equipment for cooling the fuel prior to takeoff.

The fuel losses are connected with the feed system, the speeds of the aircraft, and the characteristics of the fuels, and will depend on these factors.

5. Stability of Jet Fuels and Methods of Improving it with Antioxidant Additives

A fuel's retention of its properties under the conditions of storage and operation is known as stability.

In connection with the extremely high consumption of jet fuels, the need arises to provide certain reserves of fuel for military aviation. Fuels based on direct-distillation products may be stored for long periods, but fuels containing products of thermal cracking do not survive prolonged storage because of the presence in them of unsaturated compounds that readily form tars [resins]. In view of this, it is desirable to extend the permissible storage time for jet fuels produced by cracking and direct distillation, as is done abroad by the use of antioxidant additives. Thus, 24 g per 1 ton of an oxidation inhibitor is added to JP-3 fuel, which may contain cracking products (admissible bromine number up to 30).

As a result of increases in flight speed to 2400-3600 km/hr, the temperature of the aircraft may reach 120-330° as a result of air friction and air compression. The temperature developed in the air when it is decelerated at the surface of the aircraft is known as the decelerated-flow temperature (Table 17).

TABLE 17

Decelerated-Flow Temperature of Air at Altitude of 11 km as a Function of Flight Speed

Скорость полета, км/час 1	Температура затор- моженного потока, °C 2	Скорость полета, км/час 1	Температура затор- моженного потока, °C 2
0	—57	2400	+116
800	—32	2980	+193
1200	—13	3600	+333
1800	+41	4800	+636

1) Flight speed, km/hr; 2) decelerated-flow temperature, °C.

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The fuel in the tanks may be heated to these temperatures or to the boiling temperature.

Furthermore, the fuel may be heated in the fuel system and heat exchangers; this may result in precipitation of deposits and plugging of the fuel filters.

Consequently, fuels used in supersonic aviation are required to have high stability at a temperature of at least 150°; this figure will eventually rise to 250 to 300°. Stability of the fuel for 8 to 10 hours must be guaranteed.

The stability of the fuels depends on temperature, heating time, and the chemical composition of the fuel. Direct-distillation fuel is more or less stable up to 100°, but fuels with cracking products are not sufficiently stable. The stability of most fuels is apparently inadequate at 150, 250 and 300°.

During storage, processes associated with formation of tars, which are condensation products, may take place in the fuel under the influence of atmospheric oxygen as a result of oxidation, polymerization and condensation processes. At first, the tars remain in solution, changing the color of the fuel, but later they form precipitates that may clog the fuel filters. Tars dissolved in the fuel also result in increased carbon formation on combustion.

The relationship between the chemical properties of the fuel and its stability have not been studied with adequate thoroughness. It is known, however, that fuels containing unsaturated cracking hydrocarbons and those that contain large quantities of sulfur compounds do not have adequate stability.

The quality (as regards tar content) and stability of a fuel are determined by various methods.

At the refinery, the quality of the fuel produced and the changes

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that take place in it during storage or during thermal processing (e.g., after heating at 200°) are determined on the basis of the "actual" tar content [13] and formation of deposits.

In determining the actual tar content, 25 ml of the petroleum product to be investigated is evaporated in a beaker over an oil bath in a stream of air at 180°. After evaporation of the fuel, the tars remain and are determined by weighing on an analytical balance. The tar content in direct-distillation jet fuels of type T-1 may not exceed 10 mg per 100 ml of fuel.

The tar content in jet fuels containing cracking products (JP-3 fuel) may not exceed 20 mg per 100 ml of fuel.

Determination of the induction period is another method of characterizing the stability of fuels. The method consists in determining the time of induction during which the fuel (gasoline) being tested can stand in an oxygen atmosphere under a pressure of 7 kgf/cm^2 at a temperature of 100° and not absorb oxygen. Absorption of oxygen is determined from the pressure drop. It is conventional to assume that the initial moment of oxygen absorption coincides with the initial moment of tar formation. The duration of the induction period characterizes the tendency of the fuel to oxidize and form tars during prolonged storage. Thus, for example, it is considered that a 240-minute induction period under an oxygen pressure of 2 atmospheres (after filling a cold bomb) at 100° gives a guarantee of practically unchanged properties in cracking gasolines for 6 months. The induction period is determined in a special bomb which is placed in a boiling-water bath [14].

The stabilities of jet fuels depend on the temperature and pressure prevailing for the fuel under operational conditions or during testing. This dependence can be represented approximately in the fol-

lowing form [15]:

$$\lg \frac{\tau_1}{\tau_2} = K_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) - K_2 \lg \frac{P_1}{P_2},$$

where τ_1 is the stability (in hours) at the temperature T_1 (^{O}K) and the pressure P_1; τ_2 is the stability at the temperature T_2 and the pressure P_2.

The following values are proposed for the coefficients K:

	K_1	K_2
Jet fuel.....................	4500	0.52
Gasolines...................	5500	0.18

The material with which the fuel is in contact during production and storage is of great importance. Thus, copper has a considerable influence on the stability of fuels because soluble copper compounds which act as fuel-oxidation catalysts, even when present in "negligible" concentrations, form in the fuel.

The influence of specific hydrocarbons and mixtures of hydrocarbons on fuel stability is not sufficiently fully understood, although, as we have noted, the basic cause of low stability is the presence of unsaturated compounds in the fuel. Thus, a fuel with a high unsaturated-hydrocarbon content is most readily oxidized under the influence of molecular oxygen and forms tars.

As we noted earlier, 15-25 percent by volume of air dissolves in fuels. Oxidation of unsaturated hydrocarbons takes place preferentially at the C—H bond in the β-position with respect to the double bond, with formation of the hydroperoxide:

$$CH_2 = CH - CH_2 - CH_2 - R + O_2 \rightarrow CH_2 = CH - \underset{\underset{OOH}{|}}{CH} - CH_2 - R.$$
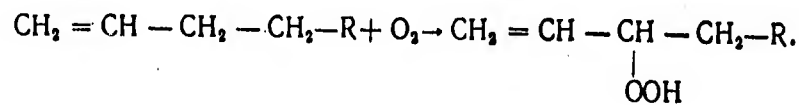
Oxidation of the unsaturated hydrocarbons is accompanied by accumulation of condensation and oxidative-condensation products, with tar formation. The greater the degree to which the hydrocarbon mixture is

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unsaturated, the higher will be its tendency to tar- and sediment formation. Cyclic olefins are more strongly inclined to oxidation reactions than open-chain olefins. Diolefins and aromatic olefins are most easily modified, undergoing oxidation and other chemical transformations.

The influence of various olefins on tar formation is listed in Table 18 for contents of 10% in the fuel.

Compounds of the styrol type, dienes, and cyclic olefins are particularly unstable during storage.

Oxidation of paraffinic hydrocarbons proceeds extremely slowly at normal storage temperatures ($+20^{\circ}$); their oxidizability increases with increasing molecular weight. Alcohols, acids, and carbonyl compounds predominate in the oxidation products of paraffins. Formation of the products of oxidative tar condensation takes place only to minimal quantities. The presence of tertiary carbon atoms increases the tendency of paraffins to oxidize and form hydroperoxides.

TABLE 18

Influence of Various Unsaturated Hydrocarbons on Tar Formation in Fuel during Storage for One Year [16]

1 Углеводород	2 Формула	Количество смол, 3 мг/100 мл
4 Стирол	$C_6H_5 - CH = CH_2$	168
5 Фенилбутадиен	$C_6H_5CH = CH - CH = CH_2$	2378
6 Диизобутилен	$CH_3 - \underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}} - CH_2 - C = CH_2$	27
7 Дипентен	$CH_3 - \bigcirc - C = CH_2$ (CH_3)	81

1) Hydrocarbon; 2) formula; 3) quantity of tars, mg/100 ml; 4) styrene; 5) phenylbutadiene; 6) diisobutylene; 7) dipentene.

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For example, 2,3-dimethylbutane readily forms the hydroxide

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_3 + O_2 \rightarrow CH_3 - \underset{\underset{OOH}{|}}{\overset{\overset{CH_2CH_3}{|}}{C}} - \underset{\underset{CH_3}{|}}{CH} - CH_3$$
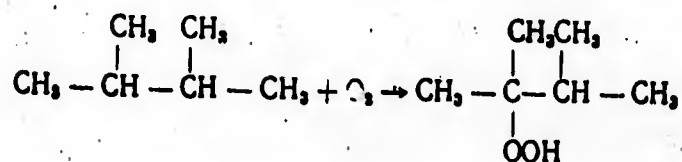
in fuel. Normal hexane undergoes conversion to the hydroperoxide with considerably greater difficulty.

Hydrocarbons with quaternary carbon atoms in the molecule possess high oxidation stability; this will be evident from the following example [16]:

Hydrocarbon	Formula	Absorption of oxygen at 120° during 6 hours of oxidation, ml/gram-molecule
Hexadecane.....................	$C_{16}H_{34}$	680
2,7-Dimethyloctane.............	$C_{10}H_{22}$	1525
2,2,4,4,6,8,8-Heptamethylnonane	$C_{16}H_{34}$	310

Naphthenic hydrocarbons have oxidizabilities that closely parallel those of the paraffinic hydrocarbons.

Naphthenic hydrocarbons with side chains oxidize more easily. Small quantities of condensation products (tars) are found in the oxidation products.

Aromatic hydrocarbons having no side chains are highly resistant to oxidation. Aromatic hydrocarbons with side chains are considerably less stable, particularly in the presence of ternary atoms, which attach oxygen easily with formation of hydroperoxides. The ability of aromatic hydrocarbons to oxidize increases with increasing number and length of side chains. Naphtheno-aromatic hydrocarbons such as tetraline react vigorously with oxygen to form hydroperoxides, which subsequently undergo conversion to products of oxidative polymerization (tars). Various condensation products (tars) form preferentially in oxidation of aromatic hydrocarbons not having side chains or having
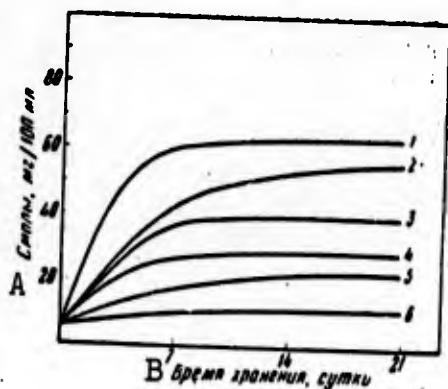
Fig. 43. Influence of various sulfur compounds on stability of fuels. On addition of various sulfur compounds (0.1% S): 1) S (elementary sulfur); 2) $C_{16}H_{33}SH$; 3) $C_{10}H_{21}SH$; 4) C_6H_5SH; 5) $C_5H_{11}SH$; 6) fuel without additives but with 0.01% S. A) Tars, mg/100 ml; 2) storage time, days.

short side chains.

Sulfur compounds, and the mercaptans in particular, increase the oxidation rates of hydrocarbons in some cases, although it is known that a number of sulfides and disulfides improve the stability of lubricating oils. The mercaptans result in considerably increased tar formation in the fuels.

Below we present a characterization of the molecular-oxygen stability of a number of hydrocarbons at 30° in the presence of 0.05% of methyl mercaptan:

Hydrocarbon	Induction period, hours
Methylcyclohexane................	80
Cumene...........................	45
Cyclohexane......................	20
Diisobutylene....................	14
Octene-1.........................	18
Methylcyclohexane 99%............ Vinylcyclohexane 1%..............	24

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Figure 43 illustrates the influence of various sulfur compounds (mercaptans and sulfur) on the stability of JP-3 jet fuel, which contains cracking products.

Below we list the stabilities of broad-fraction fuels with boiling ranges from 60 to 260° and based on direct-distillation products with various sulfur contents:

Iodine number	Sulfur content, %	Tar formation, mg/100 ml
1	0.21	8
30	0.2	21.5
52	0.23	28
30	0.4	46
16	0.87	68
12.5	0.8	118

Both unsaturated and sulfur compounds promote the accumulation of tars in the fuel.

The oxidation of fuels during storage results in the formation of unstable and reactive oxidation products (radicals, peroxides), which contribute to the development of more profound oxidation reactions. Consequently, such intermediate products are substances that contribute to autooxidation.

The presence in the fuel of a small quantity of reactive substances (phenols, aminophenols, etc.) that may react with the reactive intermediate oxidation products interrupts the oxidation process and the autocatalytic reaction does not proceed. In the presence of such antioxidant additives (oxidation inhibitors), the stability of jet fuels is improved.

The antioxidant properties of phenols in the fuels increases in the following order.

фенол резорцин флороглюцин пирокатехин гидрохи- пирогаллол
нон
— · 90 90 240 225 240
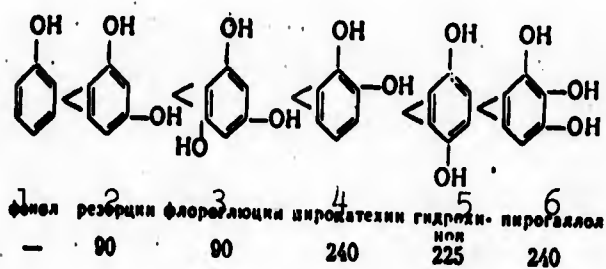
1) Phenol; 2) resorcinol; 3) floro-
glucine; 4) pyrocatechol; 5) hy-
droxyquinone; 6) pyrogallol.

The antioxidant property is less distinctly expressed in the m-
phenols than in the o- and p-diphenols.

Aromatic amino- and hydroxy compounds, such as

1 α-нафтиламин 2 β-нафтол 3 пирокатехин
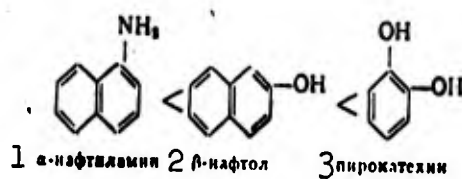
1) α-Naphthylamine; 2) β-naph-
thol; 3) pyrocatechol.

also possess antioxidant properties; however, they are less distinct
than those of the phenols. Nitro- and chlorophenols are more active
than the phenols themselves.

Among the amines tested (aniline, o-, m- and p-toluidines, xyli-
dine, o-, m- and p-nitroanilines, o-, m- and p-chloroanilines, naph-
thylamine), naphthylamine has the highest oxidation-inhibiting ability.

The presence of hydroxy and amino groups simultaneously in the
molecule increases the effectiveness of the antioxidant. Thus, n-hy-
droxydiphenylamine has much higher oxidation-inhibiting properties
than hydroquinone [18]:

- 114 -
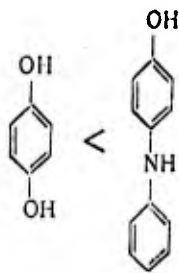
Particularly active as oxidation-inhibiting additives to fuel are alkylphenols containing alkyl radicals — usually tertiary butyl radicals — in the 2-, 4- and 6-positions with respect to the OH group. Like phenol, cresol and naphthol, nonalkylated phenols are weak antioxidants.

The oxidation-inhibiting properties of a number of alkylphenols are listed in Table 19.

Active oxidation-inhibiting additives are produced on the basis of phenols (phenol, p-cresol and xylenol) that have been alkylated with isobutylene.

Table 20 compares the activities of various antioxidant additives to jet fuels containing cracking products, in terms of their induction periods and tar formation.

Butylated aminophenols and dibutylphenylenediamine are more active as oxidation-inhibiting additives for jet fuels based on cracking products than are butylated cresols.

Aminophenols that have been alkylated in the amino group are used as oxidation inhibitors for jet fuels; an example is furfurolidene-p-aminophenol:
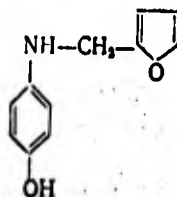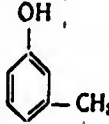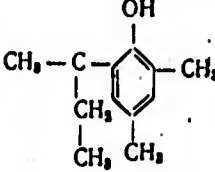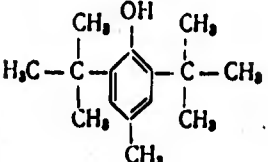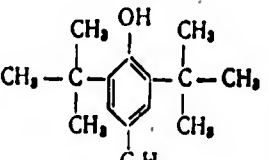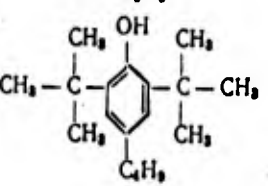
The effectiveness of the antioxidants in JP-3 fuel during a 16-hour accelerated tar test is indicated below [18, 19, 20]:

Antioxidant	Relative effectiveness
p-Butylaminophenol...............	1.0
N,N'-di-sec-butyl-p-phenylene-diamine.....................	0.55
2,6-di-tert-butyl-p-cresol.......	0.14
6-tert-butyl-p-cresol...........	0.11

TABLE 19

Oxidation-Inhibiting Properties of a Number
of Phenols [16]

1 Присадка	2 Формула	Индукционный период* 3
4 Масло без присадки	—	1
5 Фенол	OH (phenol structure)	1
6 м-Крезол	OH, CH₃ (cresol structure)	1
7 2,4-Диметил-6-втор. бутилфенол	structure	2,08
8 4-Метил-2,6-ди-трет. бутилфенол	structure	5,5
9 4-Этил-2,6-ди-трет. бутилфенол	structure	6,9
10 5-Бутил-2,6-ди-трет. бутилфенол	structure	8,0
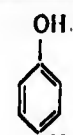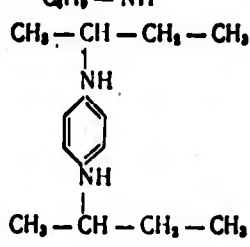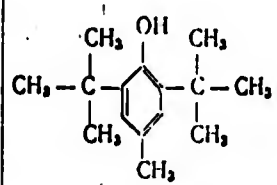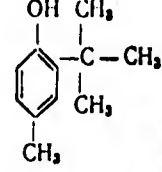
*In relative units, with reference to lubricating oil without additives.

1) Additive; 2) formula; 3) induction period*;
4) oil without additive; 5) phenol; 6) m-cresol; 7) 2,4-dimethyl-6-sec-butylphenol;
8) 4-methyl-2,6-di-tert-butylphenol; 9) 4-ethyl-2,6-di-tert-butylphenol; 10) 5-butyl-2,6-di-tert-butylphenol.

The formation of tars in the presence of various antioxidants in jet fuel containing products of thermal and catalytic cracking is illustrated by the following data [9, 13] (Table 21).

TABLE 20

Oxidation-Inhibiting Ability of Alkylated Amino-
phenols, Diamines, and Alkylphenols in Jet Fuel
[17]
(0.003% content of additive in fuel)

1 Присадка	2 Формула	3 Индукционный период, мин.	4 Относительная эффективность	
			5 по индукционному периоду	6 по образованию смол
7 л-Бутиламинофенол	[structure: phenol with C_4H_9—NH]	050	1	1
8 N,N'-Ди-втор. бутил-л-фенилендиамин	[structure: CH_3—CH—CH_2—CH_3 / NH / ring / NH / CH_3—CH—CH_2—CH_3]	670	0,53	0,51
9 Бутилированный 4-метоксифенол	—	460	0,35	0,29
10 2,6-Ди-трет.бутил-л-крезол	[structure]	200	0,12	0,13
11 2-трет. Бутил-л-крезол	[structure]	275	0,1	0,11
12 Топливо без присадки	—	200	—	—

1) Additive; 2) formula; 3) induction period, min-
utes; 4) relative effectiveness; 5) on basis of
induction period; 6) on basis of tar formation;
7) p-butylaminophenol; 8) N,N'-di-sec-butyl-p-
phenylenediamine; 9) butylated 4-methoxyphenol;
10) 2,6-di-tert-butyl-p-cresol; 11) 2-tert-butyl-
p-cresol; 12) fuel without additive.

Table 22 lists the relative efficiencies of the homologous series
of alkylphenols as antioxidants for motor fuel, on the basis of their
induction periods. Here, the oxidative [sic] effectiveness of 2,4-
dimethyl-6-tert-butylphenol is taken as unity, with the corresponding
induction period of 300 minutes [20].

Among the alkylphenols, the best antioxidants are the first three

TABLE 21

Influence of Antioxidants on Tar
Formation

1 Антиокислитель	2 Концентрация, %	3 Образование смол, мг/100 мл
4 (без присадки).	—	333
5 п-Бутиламинофенол	0,0010	36,9
	0,0035	14,7
	0,033	12,5
6 N,N'-Ди-втор. бутил-п-фениленднамин	0,0010	111,4
	0,0085	17,6
	0,033	14,4
7 2,6-Ди-трет. бутил-п-крезол	0,033	247,0
	0,0075	43,9
	0,0125	17,8
8 Бутилированный 4-метоксифенол . .	0,0015	100,4
	0,0025	23,2
	0,033	17,8
9 6-трет. Бутил-п-крезол	0,0150	5,7

1) Antioxidant; 2) concentration, %;
3) tar formation, mg/100 ml; 4) no
additive; 5) p-butylaminophenol; 6)
N,N'-di-sec-butyl-p-phenylenediamine;
7) 2,6-di-tert-butyl-p-cresol; 8)
butylated 4-methoxyphenol; 9) 6-tert-
butyl-p-cresol.

substances of those presented below:*
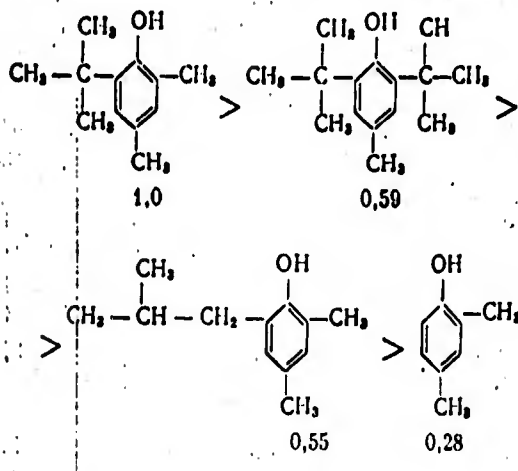
The figures under the formulas denote the relative effectiveness
of the above substances as oxidation inhibitors.

The oxidation-inhibiting abilities of a series of phenols and
phenol derivatives with respect to solid paraffinic hydrocarbons at

TABLE 22

Relative Effectiveness of Alkylphenols as Antioxidants

A Алкилфенол	В Относительная эффективность	A Алкилфенол	В Относительная эффективность
1 Фенол	0,01	23 2-Изобутил-4-метилфенол . .	0,19
2 2-Метилфенол	0,08	24 2-втор. Бутил-4-метилфенол .	0,26
3 4-Метилфенол	0,06	25 2-трет. Бутил-4-метилфенол .	0,42
4 2,4-Диметилфенол	0,28	26 2,4-Диметил-6-н. бутилфенол	0,46
5 2,6-Диметилфенол	0,21	27 2,4-Диметил-6-изобутилфенол	0,55
6 2-н. Бутилфенол	0,06	28 2,4-Диметил-6-втор. бутилфенол	0,49
7 2-Изобутилфенол	0,06	29 2,4-Диметил-6-трет. бутилфенол	1,00
8 2-втор. Бутилфенол . .	0,08	30 2,6-Диметил-4-трет. бутилфенол	0,12
9 2-трет. Бутилфенол . . .	0,14	31 2-трет.Бутил-4-н.бутилфенол	0,40
10 4-н. Бутилфенол	0,04	32 2-трет.Бутил-4-изобутилфенол	0,27
11 4-Изобутилфенол . . .	0,03	33 2-трет.Бутил-4-втор.бутилфенол	0,27
12 4-втор. Бутилфенол . .	0,03	34 2,4-Ди-трет.бутилфенол .	0,30
13 4-трет. Бутилфенол . . .	0,04	35 2,4-Ди-трет.бутил-6-метилфенол	0,28
14 2-Метил-6-н. бутилфенол .	0,14	36 2,6-Ди-трет.бутил-4-метилфенол	0,59
15 2-Метил-6-изобутилфенол . .	0,15	37 2,4,6-Три-трет. бутилфенол .	0,28
16 2-Метил-6-втор. бутилфенол .	0,17		
17 2-Метил-4-н. бутилфенол . .	0,17		
18 2-Метил-4-изобутилфенол . .	0,12		
19 2-Метил-4-втор. бутилфенол .	0,08		
20 2-Метил-4-трет. бутилфенол .	0,13		
21 2-н. Бутил-4-метилфенол . . .	0,19		
22 2-Изобутил-4-метилфенол .	0,19		

A) Alkylphenol; B) relative effectiveness; 1) phenol; 2) 2-methyl-phenol; 3) 4-methylphenol; 4) 2,4-dimethylphenol; 5) 2,6-dimethyl-phenol; 6) 2-normal butylphenol; 7) 2-isobutylphenol; 8) 2-sec-butyl-phenol; 9) 2-tert-butylphenol; 10) 4-normal butylphenol; 11) 4-iso-butylphenol; 12) 4-sec-butylphenol; 13) 4-tert-butylphenol; 14) 2-methyl-6-normal butylphenol; 15) 2-methyl-6-isobutylphenol; 16) 2-methyl-6-sec-butylphenol; 17) 2-methyl-4-normal butylphenol; 18) 2-methyl-4-isobutylphenol; 19) 2-methyl-4-sec-butylphenol; 20) 2-methyl-4-tert-butylphenol; 21) 2-normal butyl-4-methylphenol; 22) 2-isobutyl-4-methylphenol; 23) 2-isobutyl-4-methylphenol; 24) 2-sec-butyl-4-methylphenol; 25) 2-tert-butyl-4-methylphenol; 26) 2,4-dimethyl-6-normal butylphenol; 27) 2,4-dimethyl-6-isobutylphenol; 28) 2,4-dimethyl-6-sec-butylphenol; 29) 2,4-dimethyl-6-tert-butylphenol; 30) 2,6-dimethyl-4-tert-butylphenol; 31) 2-tert-butyl-4-normal butylphenol; 32) 2-tert-butyl-4-isobutylphenol; 33) 2-tert-butyl-4-sec-butylphenol; 34) 2,4-di-tert-butylphenol; 35) 2,4-di-tert-butyl-6-methylphenol; 36) 2,6-di-tert-butyl-4-methylphenol; 37) 2,4,6-tri-tert-butylphenol.

163° are listed in Table 23 [14]. The antioxidant ability of the additives was evaluated on the basis of the stabilization coefficient and the induction period, which was the time in which the peroxide number reached 50.

The stabilization coefficient is the ratio

$$k = \frac{\tau_1 - \tau_2}{A},$$

where τ_1 is the induction period of the stabilized product; τ_2 is the induction period of the unstabilized product; A is the antioxidant concentration (%).

The dihydroxynaphthalenes, their ethers, and their homologs are effective antioxidants for thermal-cracking gasoline-ligroin fractions. The oxidation-inhibiting properties of these compounds are listed in Table 24 as a function of their structure.

The effectiveness of the stabilizing action of antioxidant additives to jet fuel containing cracking products is indicated in Figs. 44 to 46.

TABLE 23

Effectiveness of Antioxidants with Respect to Solid Paraffins at 163° [21]

1 № п.п.	2 Формула	3 Концентрация, вес.%	4 Индукционный период, час.	5 Коэффициент стабилизации
1	HO—⟨⟩—C(CH₃)₂CH₃	0,1	5	40
2	HO—⟨⟩—⟨⟩	0,1	10	90
3	OH ⟨⟩—⟨⟩	0,1	4	30
4	HO—⟨⟩—C(CH₃)₂—CH₂—C(CH₃)₂—CH₃	0,01	1,5	50
5	HO—⟨⟩—C(CH₃)₃ ... C(CH₃)₃	0,01	3,5	250

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TABLE 23 (Continuation)

№ п.п.	Формула	Концентрация, вес. %	Индукционный период, час.	Коэффициент стабилизации
6	HO–C₆H₂(Br)(Br)–Br	0,01	1	0
7	HO–C₆H₂[C(CH₃)₃][C(CH₃)₃]–CH₃	0,01	5	400
8	HO–C₆H₄–NO₂	0,01	1	0
9	HO–C₆H₄–C₆H₄–OH	0,01	2,5	150
10	(OH)C₆H₄–CH₃–C₆H₄(OH)	0,01	4,5	350
11	HO–C₆H₃(OH)–CH₂–C₆H₃(OH)–OH	0,01	5	400
12	(OH)C₆H₃(Cl)–CH₃–C₆H₃(Cl)(OH)	0,01	8	700
13	(Br)(OH)C₆H₃(Br)–CH₂–C₆H₃(Br)(HO)(Br)	0,01	1	0
14	(OH)C₆H₃(NO₂)–CH₃–C₆H₃(NO₂)(OH)	0,01		(не растворим)
15	(OH)–нафтил–CH₃–нафтил–(OH)	0,01	3	200
16	HO–C₆H₄–C(CH₃)₂–C₆H₄–OH	0,01		100
17	HO–C₆H₄–CH(циклогексил)–C₆H₄–OH	0,01	1	0

TABLE 23 (Continuation)

№ п.п.	Формула	Концентрация, вес. %	Индукционный период, час.	Коэффициент стабилизации
18	(structure: bis-phenol with CH_2OH and $HOCH_2$ groups, central C–H with phenyl, two CH_3)	0,01	5	400
19	(structure: two phenol rings linked by CH_2, each with OH and CH_3)	0,01	9	800
20	(structure: three phenol rings linked by CH_2, OH and CH_3)	0,01	20	1900
21	(structure: four phenol rings linked by CH_2, OH and CH_3)	0,01	13	1200
22	(structure: polymeric $[-\text{phenol}-CH_2-]_n$ with CH_3)	0,01	7	600
23	(structure: polymeric $[-\text{phenol}-CH_2-]_n$ with phenyl)	0,01	7	600
24	(structure: catechol, OH, OH)	0,01	1	0
25	(structure: phenol with OH and OH)	0,01	2,5	150
26	(structure: resorcinol with $CH_2(CH_2)_4CH_3$)	0,01	7	600

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TABLE 23 (Conclusion)

1 № п. п.	2 Формула	3 Концентрация, вес. %	4 Индукционный период, час.	5 Коэффициент стабилизации
27		0,01	6	500
28		0,01	15	1200
29		0,01	1	0
30		0,01	18	1700
31		0,01	17	1600
31a		0,01	11	1000
32		0,01	1	0
33		0,01	8	700
34		—	—	—

1) No.; 2) formula; 3) concentration, % by weight;
4) induction period, hours; 5) stabilization coef-
ficient; 6) insoluble.

Figure 44 shows the influence of the content of the various anti-
oxidant additives on tar formation in a 16-hour accelerated test.

Figure 45 presents data on the kinetics of tar formation in fuel
in the presence of 0.0033% of the various antioxidants.

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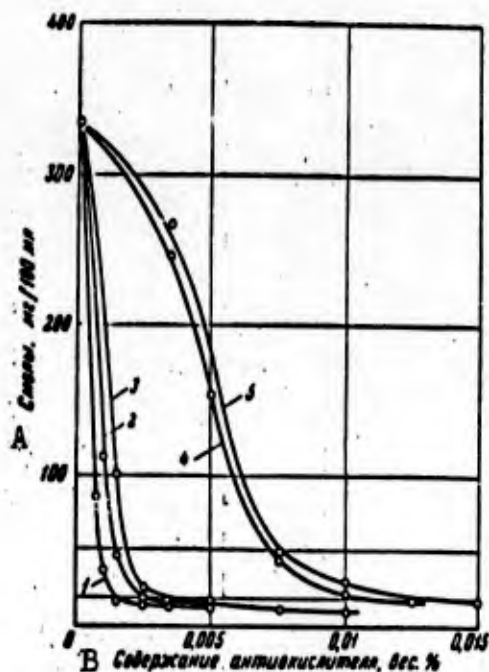
Fig. 44. Influence of antioxidant additives on tar formation in jet fuel containing cracking products, during 16-hour accelerated test. 1) p-butylaminophenol; 2) N,N'-di-sec-butyl-p-phenylenediamine; 3) butylated 4-methoxyphenol; 4) 2,6-di-tert-butyl-p-cresol; 5) 6-tert-butyl-p-cresol. A) Tars, mg/100 ml; B) antioxidant content, % by weight.
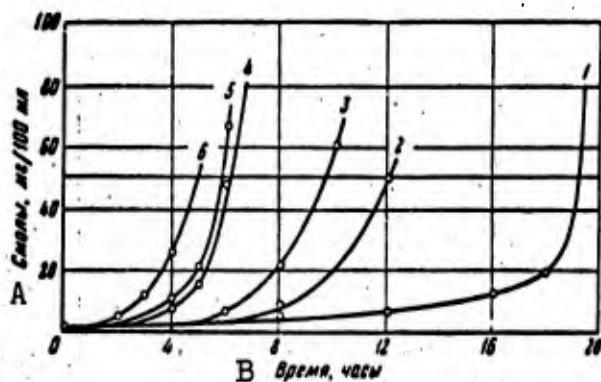
Fig. 45. Influence of various antioxidants taken in quantities of 0.0033%, on tar-formation kinetics. 1) p-aminophenol; 2) N,N'-di-sec-butyl-p-phenylenediamine; 3) butylated 4-methoxyphenol; 4) 2,6-di-tert-butyl-p-cresol; 5) 6-tert-butyl-p-cresol; 6) control experiment. A) Tars, mg/100 ml; B) time, hours.

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TABLE 24

Antioxidant Effectiveness of Dihydroxynaphthalenes
and Their Ethers and Homologs on Addition to
Thermal-Cracking Gasoline [22]
(Antioxidant concentration 0.025%)

1 Наименование	Индукционный период, 2 мин.	1 Наименование	Индукционный период, 2 мин.
3 1,2-Диоксинафталин ...	40	14 1-Окси-5-метоксинафталин .	815
4 1,3-Диоксинафталин ...	5	15 1-Окси-5-этоксинафталин ..	790
5 2-Метил-1,4-диоксинафталин	0	16 1-Окси-7-метоксинафталин ..	905
		17 2-Окси-6-метоксинафталин ..	365
6 1,5-Диоксинафталин ...	1110	18 2-Окси-1-метоксинафталин ..	90
7 1,6-Диоксинафталин ...	305	19 1-Окси-6-метоксинафталин ..	155
8 1,7-Диоксинафталин ...	1315	20 1-Окси-8-метоксинафталин .	20
9 1,8-Диоксинафталин ...	110	21 2-Окси-3-метоксинафталин .	25
10 2,3-Диоксинафталин ...	10	22 1-Метокси-4-оксидигидро-нафталин ...	780
11 2,6-Диоксинафталин ...	750		
12 2,7-Диоксинафталин ...	45	23 1-Метокси-5-окси-5,6,7,8-тетрагидронафталин ...	850
13 1-Окси-2-метил-4-метокси-нафталин ...	190		

1) Name; 2) induction period, minutes; 3) 1,2-
dihydroxynaphthalene; 4) 1,3-dihydroxynaphthalene;
5) 2-methyl-1,4-dihydroxynaphthalene; 6) 1,5-
dihydroxynaphthalene; 7) 1,6-dihydroxynaphthalene;
8) 1,7-dihydroxynaphthalene; 9) 1,8-dihydroxynaph-
thalene; 10) 2,3-dihydroxynaphthalene; 11) 2,6-
dihydroxynaphthalene; 12) 2,7-dihydroxynaphthalene;
13) 1-hydroxy-2-methyl-4-methoxynaphthalene; 14)
1-hydroxy-5-methoxynaphthalene; 15) 1-hydroxy-5-
ethoxynaphthalene; 16) 1-hydroxy-7-methoxynaphtha-
lene; 17) 2-hydroxy-6-methoxynaphthalene; 18) 2-
hydroxy-1-methoxynaphthalene; 19) 1-hydroxy-6-
methoxynaphthalene; 20) 1-hydroxy-8-methoxynaph-
thalene; 21) 2-hydroxy-3-methoxynaphthalene; 22)
1-methoxy-4-hydroxydihydronaphthalene; 23) 1-
methoxy-5-hydroxy-5,6,7,8-tetrahydronaphthalene.

Figure 46 shows the influence of the nature and quantity of the
additives on the induction period.

Among the additives tested, p-butylaminophenol is the most ef-
fective.

Copper deactivators are added to the antioxidants to improve

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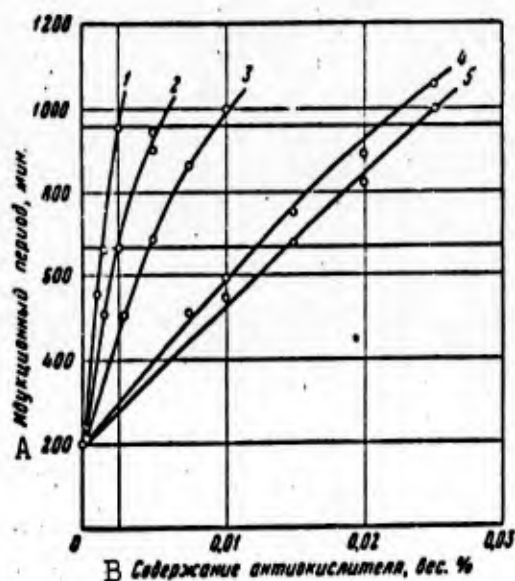
Fig. 46. Influence of nature
and quantity of additives on
induction period of jet fuel
with cracking products. 1) p-
butylaminophenol; 2) N,N'-di-
sec-p-butyl-p-phenylenediamine:
3) butylated 4-methoxyphenol;
4) 2,6-di-tert-butyl-p-cresol;
5) 6-tert-butyl-p-cresol. A)
Induction period, minutes; B)
antioxidant content, % by
weight.

their effectiveness. Thus, the deactivator disalicylidene-1,2-propane-
diamine (0.0013%) is added to p-butylaminophenol (0.0033%).

Other additives included in the fuel to improve its storage sta-
bility and to prevent formation of deposits on heating are listed in
Table 25 together with anticorrosion additives [23, 24].

6. Stability of Jet Fuels at High Temperatures (Thermal Stability)
[6, 23, 25-29]

In contemporary reaction-thrust engines — turbojet, ramjet, and
liquid rocket engines — the fuel is used to cool the engine, and in
turbojet engines it is also used to cool the oil of the engine system.

The fuel in the tanks of an aircraft may be heated at high flight
speeds. Thus, at an altitude of 11 km, the temperature attained on de-
celeration of the air at the surface of the aircraft may reach the fol-

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lowing values at various flight speeds:

$$1200 \text{ km/hr}\ldots\ldots\ldots\ldots 30^\circ C$$
$$2400 \text{ km/hr}\ldots\ldots\ldots\ldots 130^\circ C$$
$$3600 \text{ km/hr}\ldots\ldots\ldots\ldots 330^\circ C$$
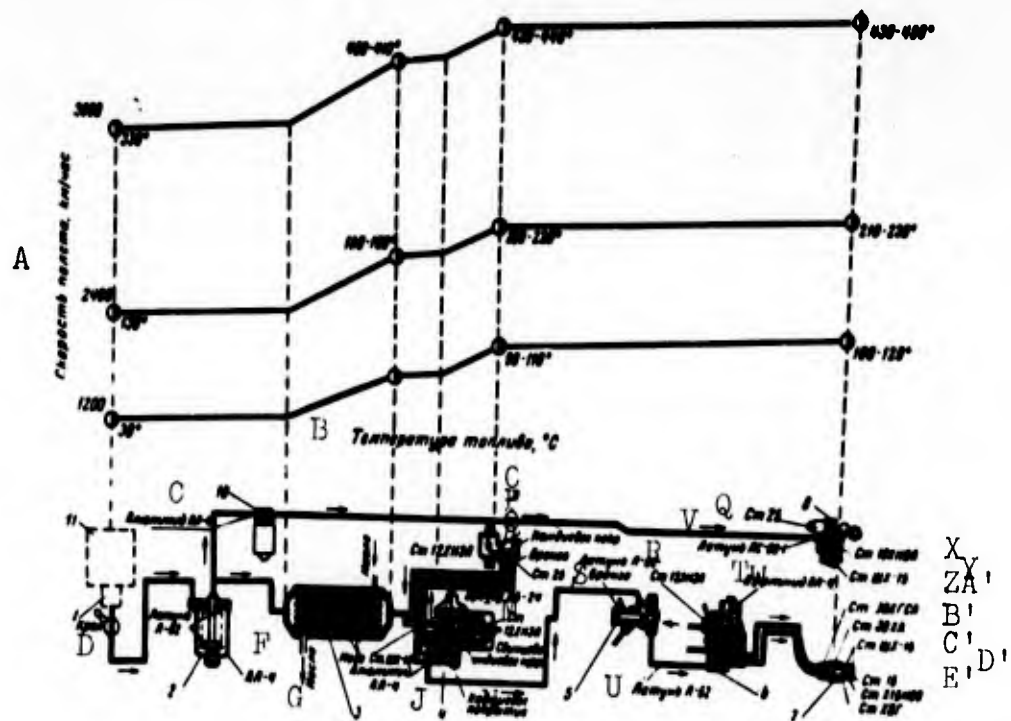
Fig. 47. Variation of fuel temperature in fuel system of jet engine as a function of flight speed.
1) Transport pump; 2) filter; 3) fuel-oil radiator; 4) pump; 5) throttling valve; 6) distributor; 7) nozzle; 8) starting igniter; 9) barostat; 10) priming pump; 11) fuel tank. A) Flight speed, km/hr; B) fuel temperature, °C; C) aluminum AL-4; D) cock; E) brass L-62; F) AL-4; G) oil; H) copper; I) St. ShKh-15; J) aluminum AL-4; K) St. 12KhN3A; L) bronze VB-24; M) lead-indium coating; N) cadmium coating; O) cadmium coating; P) bronze; Q) St. 25; R) brass L-62; S) bronze; T) St. 12KhN3A; U) brass L-62; V) brass LS-59-1; W) aluminum AL-4; X) St. 18KhN6A; Y) St. ShKh-15; Z) St. 30KhGSA; A') St. 38KhA; B') St. ShKh-15; C') St. 15; D') St. Kh15N... [illegible]; E') St. KhVG.

In passing through the engine's fuel system, the fuel is heated by about another 100°. The variation of fuel temperature in the fuel system of a jet engine as a function of flight speed is shown in Fig. 47.

TABLE 25

Fuel Additives [24]

1 Название	2 Формула	3 Концентрация, %	4 Назначение
	5 Антиокислительные присадки		
6 Бутилоктадециламин	$C_{18}H_{37}NHC_4H_9$	0,003—0,06	18 Для бензинов
7 Дибутилоктадециламин	$C_{18}H_{37}N(C_4H_9)_2$		
8 Смесь алкиламинов	$C_8 - C_{10} - NH_2$		19 То же » » »
9 N-Лаурилбутилендиаминостеарат	$C_{17}H_{35}COOHNH_2(CH_2)_4NHC_{12}H_{24}$	0,0001	
10 л-Фенилендиамин	$C_6H_4(NH_2)_2$	0,001—0,1	
11 N,N'-Диметил-л-фенилендиамин	$C_6H_4(NHCH_3)_2$	0,1	20 Для крекинг-бензинов
12 N,N'-Диизопропилен-л-фенилендиамин	$C_6H_4(NHC_3H_7)_2$	0,001	19 То же
13 Циклогексилфенил-л-фенилендиамин	$C_6H_5NHC_6H_4NHC_6H_{11}$	0,001	» »
14 N,N'-Ди-втор. бутил-л-фенилендиамин	$C_6H_4(NHC_4H_9)_2$	0,2	
15 Гексаметилтриамино-2,4,6-метиленфенол		—	18 Для бензинов
16 S-бензилтиомочевина		0,001—1,0	21 Для бензинов с крекинг-компонентом
17 1,3-Дигексил-5-нитро-5-пропилгексагидропиримидин		—	22 Для керосинов

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TABLE 25 (Continuation)
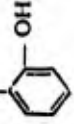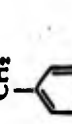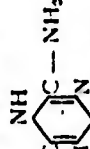
1 Название	2 Формула	3 Концентрация, %	4 Назначение
	23 *Дезактиваторы металлов*		
24 Дисалицилиденэтилендиамин	HC = N — CH₂ — CH₂ — N = CH (с фенольными кольцами, HO—, —OH)	0,01—0,001	32 Для дистиллятов, кипящих в пределах 200—400°
25 Салицилиденаминофенол	(фенольное кольцо, OH, HO)	—	33 Для топлив, содержащих крекинг-компоненты
	26 *Присадки для уменьшения осадкообразования*		
27 Алифатические амины с одной или большим числом алкильных групп C₁₄ — C₁₈	C₁₂H₂₅NH₂, C₁₄H₂₉NH₂, C₁₆H₃₃NH₂	0,0005—0,015	34 Для дистиллятных топлив
28 Первичные алифатические амины;	$R-\overset{R}{\underset{R}{C}}-NH_2$	—	
29 Третичные алифатические амины C₉ — C₂₀	$H(-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-)_n-N=CH_2$	0,005—0,2	35 Для топлив, кипящих выше 150°
30 Формальдегидимины			19 То же
31 Аминоспирты с 6—20 атомами углерода	$H_2N-CH_2-\underset{OH}{CH}-R$	0,0014—1,0	» »

TABLE 25 (Conclusion)

1 Название	2 Формула	3 Концентрация, %	4 Назначение
36 Диметилалкилбензилсульфоэтиламмоний	CH_3 $CH_3 — NH — C_2H_4SO_3H$ CH_2 — (бензольное кольцо) — R	—	46 Против осадкообразования и коррозии
37 Моноэфир полиэтиленгликоля и жирной кислоты $C_{12} — C_{22}$	$HO[— C_2H_4O —]_xC_2H_4OCOR$		47 Для предотвращения забивки топливоподающей системы авиационных газовых турбин
38 2-Амино-4-н.пропил-6-додецилфениламино-1,4-дигидротриазин	$C_{12}H_{25}C_6H_4NH — C \overset{NH}{\underset{\underset{CH — C_3H_7}{N}}{}} C — NH_2$	0,001—0,1	48 Для ... чзинов
39 *Антикоррозийные присадки*			
40 Циклогексиламмониевая соль алкилсульфаминоуксусной кислоты	$RSO_2NHCH_2COOH·NH_2C_6H_{11}$	0,025—0,1	48 Для бензинов
41 Алкилфенол в смеси с карбоновой кислотой			19 То же
19 То же			
42 Диалкоксидиаминосилан	$(RO)_2Si(NH_2)_2$ $(R = C_nH_{2n+1}, \; n = 1—20)$	0,002—0,05 0,001—0,5	49 Ингибитор коррозии железа
43 Диэтилтиомочевина	$(C_2H_5)_2 N — CS — NH_2$		
44 Дибутилдитиоацетат	$C_4H_9OOCCH_2 — S — S — CH_2COOC_4H_9$	0,025	50 Ингибитор коррозии медных деталей
45 Продукты реакции жирных аминов с кислотами		0,5	51 Ингибитор коррозии черных металлов

Key to Table 25

1) Name; 2) formula; 3) concentration, %; 4) use; 5) antioxidant additives; 6) butyloctadecylamine; 7) dibutyloctadecylamine; 8) mixture of alkylamines; 9) N-lauryl butylenediamine stearate; 10) p-phenylenediamine; 11) N,N'-dimethyl-p-phenylenediamine; 12) N,N'-diisopropylene-p-phenylenediamine; 13) cyclohexylphenyl-p-phenylenediamine; 14) N,N'-di-sec-butyl-p-phenylenediamine; 15) hexamethyltriamino-2,4,6-methyl-enephenol; 16) S-benzylthiourea; 17) 1,3-dihexyl-5-nitro-5-propylhexa-hydropyrimidine; 18) for gasolines; 19) same; 20) for cracking gasolines; 21) for gasolines with cracking component; 22) for kerosenes; 23) metals deactivators; 24) disalicylidene ethylenediimine; 25) salicylidene aminophenol; 26) additives to reduce scaling; 27) aliphatic amines with one or more alkyl groups $C_{14}-C_{18}$; 28) primary aliphatic amines; 29) tertiary aliphatic amines C_8-C_{20}; 30) formaldehyde imines; 31) aminoalcohols with 6-20 carbon atoms; 32) for distillates boiling in range from 200 to 400°; 33) for fuels containing cracking components; 34) for distillate fuels; 35) for fuels boiling above 150°; 36) dimethylalkylbenzylsulfoethyl ammonia; 37) monoether of polyethylene glycol and fatty acid C_{12} to C_{22}; 38) 2-amino-4-normal propyl-6-dode-cylphenylamino-1,4-dihydrotriazine; 39) anticorrosion additives; 40) cyclohexylamine salt of alkylsulfaminoacetic acid; 41) alkylphenol mixed with carboxylic acid; 42) dialkoxydiaminosilane; 43) diethyl thiourea; 44) dibutyl dithioacetate; 45) products of reaction between aliphatic amines and acids; 46) antiscaling and anticorrosion; 47) to prevent plugging of fuel-feed system in aviation gas turbines; 48) for gasolines; 49) inhibits corrosion of iron; 50) inhibits corrosion of copper components; 51) inhibits corrosion of nonferrous metals.

By thermal stability of a fuel, we mean minimum tendencies on the part of the fuel toward:

1) formation of insoluble-particle deposits that may plug the fuel filters in air-breathing engines, with a resulting drop in fuel flow rate;

2) depositing a dense film of tars on the cooled surfaces of the engine. This reduces the cooling effect and may, in liquid-fuel rocket engines, where the combustion temperature is very high, result in the wall of the engine burning through.

The formation of resinous substances and deposits takes place as a result of the effects of elevated temperatures and atmospheric oxygen on the fuel.

One of the factors resulting in formation of precipitates is composed of the oxidation processes of the most reactive sulfurous and nitrogenous substances and the condensation processes of tars that are soluble in the fuel. Bicyclic aromatic compounds — naphthalene and its derivatives — may be sources of deposit formation.

Several techniques have been developed for investigation of the thermal stability of fuels [6].

The first method is based on heating the fuel at temperatures up to 150° (temperature deviation $\pm 0.5^\circ$) in a glass container with air given free access. Plates made from the metals with which the fuel comes into contact in the engine and having the dimensions 40 x 10 x 2 mm are suspended in the container. The fuel container communicates with the atmosphere through a reflux container. The fuel is agitated during the six-hour test period.

After the test, the fuel is cooled and filtered through a No. 4 glass filter. The insoluble deposits remain on the filter, are washed off with isopentane, dried to constant weight, weighed, and the result

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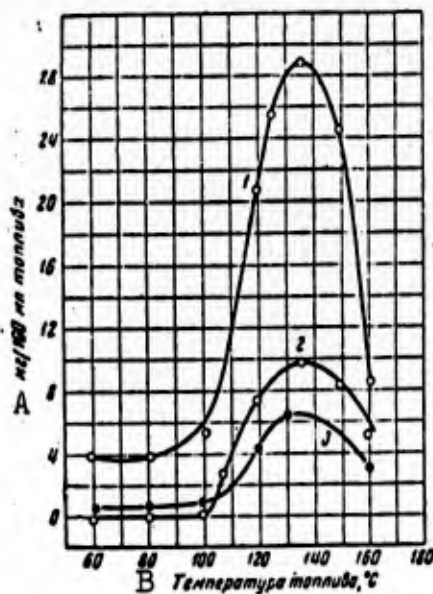
Fig. 48. Formation of soluble tars and deposits in T-1 fuel at various temperatures. 1) Formation of actual resins, mg/100 ml of fuel; 2) formation of deposits, ml/100 ml of fuel; 3) acidity, mg of KOH per 100 ml of fuel. A) mg/100 ml of fuel; B) temperature of fuel, ^{o}C.

converted to the weight of the insoluble residue in milligrams per 100 ml of fuel.

A second technique has been developed for testing thermal stability to a temperature of 150 or 300° under pressure in a bomb or glass container.

A method for testing fuels at elevated temperatures with continuous passage of air has been proposed.

The investigations carried out indicated that almost all fuels have their scale-formation and tar-accumulation maxima at a temperature of about 130-150°, after which the deposition of solid particles diminishes. This will be evident from Fig. 48.

Another apparatus for evaluating the thermal stability of fuels reproduces the fuel system of a supersonic aircraft (Fig. 49).

The fuel to be tested is poured into the tank of the experimental

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apparatus, from which it is pumped under a pressure of 10 atmospheres and at a rate of 1.8-2.0 kg/hr through a special filter with 20-μ pores. Before the filter, the fuel is heated to a temperature of 150°. The difference in pressures before and after the filter changes as deposits are built up on its surface. In this method, a fuel is regarded as stable if the pressure difference does not exceed 50 mm of mercury after five hours.

According to the USA's specifications for gas-turbine fuel, a fuel is regarded as stable if the maximum pressure difference does not exceed 305 mm of mercury after five hours of pumping the fuel, which has been heated to 149°, through a filter whose temperature is held at 204° at a rate of 2.7 kg/hr.

Deposits formed by various fuels in thermal-stability determinations are listed in Table 26.

The composition of the deposits formed is of considerable interest. Research has shown that the oxygen content amounted to 20-50% and that of sulfur 5 to 10%. This indicates that the deposits were formed chiefly by the soluble tars and oxygen and sulfur compounds in the fuel. Thus, the quantity of sulfur-containing compounds reaches 1-1.2% in TS-1 fuel when analysis shows a sulfur content of 0.2 to 0.25%.

The sediment represents a product of profound oxidative transformation of low-stability hydrocarbons and sulfur, oxygen and nitrogen compounds. They form as a result of oxidation of these compounds by atmospheric oxygen and subsequent condensation of the oxidation products to resinous and then to solid encrustations.

Sediment compositions are given in Table 27.

The composition of the ash includes metals, for the most part copper, in quantities ranging from 20 to 65%. The metals enter the deposits as a result of corrosion.

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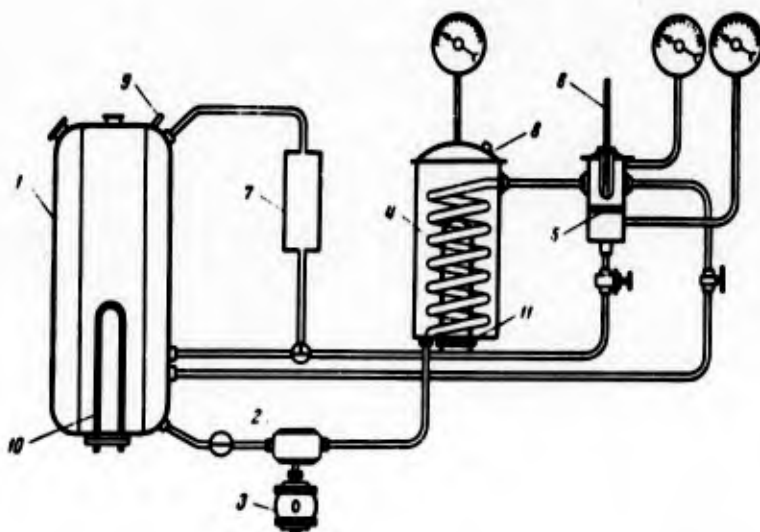
Fig. 49. Diagram of apparatus for determining thermal stability of fuels. 1) Tank; 2) pump; 3) motor; 4) coil; 5) filter; 6) thermometer; 7) fuel flowmeter; 8,9) reducing valves; 10,11) heater or cooler.

TABLE 26

Sedimentation and Tarry Deposits Formed by Fuels in Determination of Thermal Stability at 120°

1 Топливо	2 Образование осадков, мг/100 мл			6 Образование отложений, мг/м²
	3 без металла	4 сталь Х-18	5 бронза	
T-1	5	7	24	1000
T-2	7 Нет	7 Нет	24	1200
8 TC-1	2	—	—	—
9 Крекинг- керосин	18	22	32	1500

1) Fuel; 2) sedimentation, mg/100 ml; 3) without metal; 4) Kh-18 steel; 5) bronze; 6) deposit formation, mg/m^2; 7) none; 8) TS-1; 9) cracking kerosene.

Characterization of the thermal stability of the fuels based on tests run with this apparatus gives a correct comparative evaluation of their behavior in the engine, as will be seen from the following:

TABLE 27

Composition of Sediments Precipitated
on Heating Fuels to 150°

1 Топливо	2 Состав осадков, %					
	C	H	S	N	O	зола 3
T-1	33,73	3,41	5,90	1,03	46,56	7,28
4 TC-1	29,10	3,36	8,14	0,67	49,68	7,05

1) Fuel; 2) sediment composition, %;
3) ash; 4) TS-1.

Time for increase of pressure difference to 50 mm Hg	Time after which filter blocks up in aircraft
25 min....................3 hours	
100 min....................8 hours	

There are several possible ways of producing fuels that possess
high thermal stability:

1) elimination of chemically active sulfur and resinous substances,
which contribute to the formation of deposits;

2) selection of the most favorable hydrocarbon composition, which
will include the most stable hydrocarbons;

3) introduction of additives that improve the thermal-oxidation
resistance of the fuels;

4) introduction of additives that disperse precipitates to a
state in which they are not trapped by the filter.

Purification of aviation fuels with sulfuric acid, sulfuric anhy-
dride, or adsorbents (silica gel, aluminum oxide) and, in particular,
hydrolytic purification improve the thermal stability of fuels.

Thus, when aviation kerosene was purified with sulfuric acid, its
thermal stability was raised from 100 to 300 minutes, and selective
extraction of sulfur-containing and resinous compounds with liquid
sulfuric anhydride raised it from 100 to 200 minutes.

Vapor-phase purification of another batch of fuel over aluminum

oxide raised its thermal stability from 30 to 245 minutes.

Hydrolytic purification is regarded as the most effective method of purifying aviation fuels.

In the USA, preference is accorded to this method. In that country in 1958, the total plant capacity for hydrolytic purification came to over 53 million tons, and by 1962 it is expected to reach about 95 million tons.

Another possible way of reducing deposit formation is the introduction into the fuel of additives that inhibit oxidation processes, since the formation of insoluble tars is a consequence of oxidation processes.

Additives that reduce deposit formation may be classed into the following groups.

1) Aliphatic amines, for example

$$R-\overset{\displaystyle R_1}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-NH_2,$$
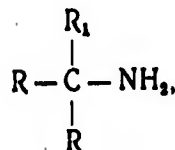
where R is a radical from C_8H_{17} to $C_{20}H_{41}$ and R_1 is a CH_3 or C_3H_7 radical.

2) Formaldimines of the type

$$H\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\right)_n N=CH_2,$$
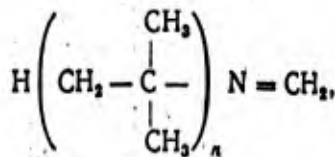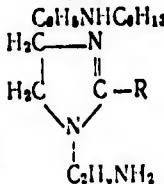
where n = 1 to 6.

3) Condensation products formed by triethanolamine with alcohols or fatty acids and other compounds containing amino groups.

Experimental testing of various additives — embracing over 100 compounds — indicated that the most effective are aliphatic amines from C_{10} to C_{40}; additives belonging to the triethanolamine group and

TABLE 28

Influence of Additives on Thermal
Stability of Fuels at 120° in Contact
with Bronze Plate [23]

1 Присадка	2 Формула	3 Образование осадка, мг/100 мл
4 Топливо Т-2 в смеси с 30% крекинг-компонента		
6 Без присадки		0
7 Алифатические амины C₁₀ — C₄₀	$(R)_3N$	1
8 Полиэтиленполиамин . .	$(H_2NC_2H_4NHC_2H_4-)_xNH_2$	6
9 Соль триэтаноламина и жирных кислот	$(HOC_2H_4)_3N \cdot HOOCR$	2—3
5 Топливо ТС-1, содержащее 0,045% меркаптановой серы		
10 Без присадки		20
11 Алифатические амины C₁₀ — C₄₀	$(R)_3N$	3
12 Моногексиланилин . . .	$C_6H_5NHC_6H_{13}$	4
13 Аминоэтилалкилимид-азолин	H_2C-N structure $H_2C\quad C-R$ N $C_2H_4NH_2$	1

1) Additive; 2) formula; 3) formation
of deposit, mg/100 ml; 4) T-2 fuel
mixed with 30% of cracking component;
5) TS-1 fuel containing 0.045% of
mercaptan sulfur; 6) no additive; 7)
aliphatic amines C_{10} to C_{40}; 8) poly-
ethylenepolyamine; 9) salt of tri-
ethanolamine and fatty acids; 10) no
additive; 11) aliphatic amines, C_{10}
to C_{40}; 12) monohexylaniline; 13)
aminoethylalkylimidazoline.

Fig. 50. Microphotographs of deposits formed by
JP-4 turbojet fuel before and after heat treatment.
1) Fuel before heating; 2) fuel after heating; 3)
fuel after heating in presence of 0.02% of dis-
persing additive.

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TABLE 29

Thermal Stability of T-1 Fuel at 150° during 2-Hour Test in Presence of 0.05% of Additive [30]

| 1 Присадка | 2 Формула | 3 Количество осад. кл, мг/100 мл | |
		4 без металла	5 с медной пластинкой
6 Без присадки	—	7,7	8,3
7 2-Амино-4-пропилфенол	$C_6H_3(OH)(NH_2)(C_3H_7)$	2,8	5,1
8 2-Амино-4-трет.бутилфенол	$C_6H_3(OH)(NH_2)(C_4H_9)$	1,3	3,9
9 2-Амино-4-трет.амилфенол	$C_6H_3(OH)(NH_2)(C_5H_{11})$	1,0	2,5
10 2,6-Диамино-4-трет.бутилфенол	$H_2N-C_6H_2(OH)(NH_2)(C_4H_9)$	3,7	2,0

1) Additive; 2) formula; 3) quantity of deposit, mg/100 ml; 4) without metal; 5) with copper plate; 6) without additive; 7) 2-amino-4-propylphenol; 8) 2-amino-4-tert-butylphenol; 9) 2-amino-4-tert-amylphenol; 10) 2,6-diamino-4-tert-butylphenol.

incomplete esters of monobasic alcohols with fatty acids show lower effectiveness.

The influence of additives on deposit formation in fuels is shown in Table 28.

Another group of additives that reduce deposit formation is the amylaminophenols. The results of using these additives at 150° in the presence of copper plates are shown in Table 29 [30].

Thus, the alkylaminophenols reduce deposit formation considerably

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in T-1 fuel.

Another trend taken in improving the quality of fuel as regards deposit formation is the introduction into the fuel of special dispersing additives that prevent precipitation of the deposits in the form of large particles and an insoluble tar, and remain in the fuel in the form of very finely dispersed particles that are easily filtered without plugging the filter.

Figure 50 shows microphotographs of deposits of JP-4 fuel prior to heat treatment, after heat treatment in the absence of dispersing additives, and with 0.02% of a dispersing additive.

The experiments were run on a special apparatus that simulates the application of the fuel.

Most stable with respect to tar formation are fuels produced by hydrolytic cracking (e.g., JP-5 fuel), which are stable for a relatively long time at 200-250° [8].

The stability of fuels can be raised by thorough purification with sulfuric acid, sulfuric anhydride and adsorbents, such as activated aluminum oxide, and by hydrolytic purification [31, 32].

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Manu- script Page No.	[Footnote]
118	Pentamethylphenol has also been proposed as an effective antioxidant.

Chapter 3

HYDROCARBON COMPOSITION AND PHYSICOCHEMICAL PROPERTIES OF CRUDE PETROLEUM FOR THE PRODUCTION OF REACTION FUELS

1. Composition of Petroleums and Gasoline-Kerosene Fractions from the Direct Distillation of Petroleum

Petroleums from various districts, as well as products from the heat treatment of petroleum distillates and residues serve as the basic raw material for the production of reaction fuels.

The yield of fuel from petroleum depends in great measure on the properties of the petroleum and the requirements which are imposed on the fuel with respect to fractional composition and pour point. The hydrocarbon composition of the gasoline-kerosene fractions of the petroleum affect the quality of the fuels, as do the content and type of the sulfur compounds. The potential quantities of reaction fuels in petroleum are determined by the fractional composition of the petroleum and the properties of the hydrocarbons boiled over, approximately, between 65 and 300°. Conventional kerosene fractions are used for the production of reaction fuel; gasoline fractions are used in the case of fuels exhibiting an expanded fractional composition.

Table 30 presents the characteristics of the petroleums from various deposits. Particular attention should be devoted to the yield of fractions boiling over below 300°, i.e., the $150-300^{\circ}$ fractions which determine the potential availability of fuels in the given petroleum. However, the yield of fuel from the petroleum cannot be estimated unless the actual pour points are taken into consideration. The

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TABLE 30

Characteristics of Petroleums from Various Deposits [1, 2]

1 Нефть	2 Плотность	3 Т. заст., °С	4 Содержание серы, %	5 Потенциальное содержание фракции, %			
				6 до 150°	150—200°	200—300°	до 300°
7 Район Второго Баку							
8 Ишимбаевская	0,87	—20	2,68	15	9	16	40
9 Туймазинская (угленосная свита)	0,89	—20	3,2	10	6	17	33
10 Туймазинская (девонская)	0,85	—59	1,5	17	8	16	41
11 Чусовская	0,94	—30	5,9	19	7	12	38
12 Ухтинский район							
13 Ухтинская (III горизонт)	0,93	—20	1,24	—	—	10	10
14 Бакинский район							
15 Сураханская (обыкновенная)	0,85	—	0,15	—	31	—	39
16 Бинагадинская	0,86	—	0,33	—	25	—	29
17 Грозненский район							
18 Парафинистая	—	—	0,2	—	26	—	36
19 Беспарафинистая	—	—	0,33	—	24	—	—
20 Эмбенский район							
21 Доссорская нефть (I горизонт)	0,837	—50	0,18	—	30	—	45

1) Petroleum; 2) density; 3) pour point, °C; 4) sulfur content, %; 5) potential content of fraction, %; 6) up to 150°; 7) Second Baku Rayon [District]; 8) Ishimbay; 9) Tuymazy (Carboniferous strata); 10) Tuymazy (Devonian); 11) Chusovoy; 12) Ukhta Rayon [District]; 13) Ukhta (III-rd level); 14) Baku District; 15) Surakhany (conventional); 16) Binagadi; 17) Grozno District; 18) paraffin-base petroleum; 19) nonparaffin-base petroleum; 20) Emba District; 21) Dossor petroleum (I-st level).

sulfur content is also a significant characteristic, since it in great measure determines the quality of the fuel obtained from the petroleum.

It follows from Table 30 that the potential content of fractions boiling over below 300° does not exceed 40% in the majority of cases, and the content of the kerosene fraction (150-300°) does not exceed 25%

TABLE 31

Group Composition of Kerosene Fractions from Petroleums of Various Deposits [1, 2]

1 Нефть	3 парафиновые			4 нафтеновые			5 ароматические		
	150—200°	200—250°	250—300°	150—200°	200—250°	250—300°	150—200°	200—250°	250—300°
6 *Бакинский район*									
7 Сураханская (отборная)	17	38	45	66	44	39	17	18	16
8 Бибиэйбатская	7,9	10,1	10,6	69	51	42	12	22	27
9 *Грозненский район*									
10 Парафинистая	57	59	61	29	23	22	14	18	17
11 Беспарафинистая	24	11	8	55	63	59	21	26	33
12 *Эмбенский район*									
13 Доссорская (юрская)	16	28	20	80	64	68	4	8	12
14 *Район Второго Баку*									
15 Ишимбаевская	49	38	41	28	35	26	23	27	33
16 Туймазинская	58	50	37	21	25	40	21	25	23

(column group header: 2 Содержание углеводородов во фракциях, %)

1) Petroleum; 2) content of hydrocarbons in the fractions, %; 3) paraffinic; 4) naphthenic; 5) aromatic; 6) Baku District; 7) Surakhany (top grade); 8) Bibieybatskaya; 9) Grozno District; 10) paraffin-base petroleum; 11) nonparaffin-base petroleum; 12) Emba District; 13) Dossor (Jurassic); 14) Second Baku District; 15) Ishimbay; 16) Tuymazy.

TABLE 32

Group Composition of Fractions from Various Petroleums Boiling over below 200° [2]

1 Нефть	3 ароматические	4 нафтеновые	5 метановые
6 Ишимбаевская	16	24	60
7 Туймазинская	10	21	69
8 Чусовская	46	24	30
9 Сызранская	15	27	58
10 Бугурусланская	23	15	62

(column group header: 2 Содержание углеводородов, %)

1) Petroleum; 2) content of hydrocarbons, %; 3) aromatic; 4) naphthenic; 5) methane; 6) Ishimbay; 7) Tuymazy; 8) Chusovoy; 9) Syzran'; 10) Buguruslan.

TABLE 33

Characteristic of Kerosene Distillates of Petroleum [1-3]

1 Нефть	Плотность при 20° 2	Содержание серы, % 3	Фракционный состав, °C 4		Выход фракция на нефть, % 5	
			н. к. 6	к. к. 7	до к. к. 8	н. к.—до 200° 9
10 Район Второго Баку						
11 Ишимбаевская	0,827	1,0	169	310	25,3	21
12 Туймазинская (угленосная свита)	0,824	1,84	165	312	27,7	24
13 Туймазинская (девонская) . .	0,817	0,71	180	290	28,5	20
14 Чусовская	0,876	2,60	165	311	23,3	20
15 Эмбенский район						
16 Доссорская	0,836	—	150	314	50	20
17 Макатская	0,869	0,02	215	280	—	—
18 Средняя Азия						
19 Небитдагская	0,84	—	154	313	30	20,5

1) Petroleum; 2) density, at 20°; 3) sulfur content, %; 4) fractional composition, °C; 5) yield of fraction, %, of petroleum; 6) start of boiling; 7) end of boiling; 8) prior to end of boiling; 9) start of boiling below 200°; 10) Second Baku District; 11) Ishimbay; 12) Tuymazy (Carboniferous strata); 13) Tuymazy (Devonian); 14) Chusovoy; 15) Emba District; 16) Dossor; 17) Makat; 18) Central Asia; 19) Nebit-Dag.

TABLE 34

Content of Sulfur and Sulfur Compounds in Fractions of Various Petroleums Boiling below 200° [1-3]

1 Нефть	Содержание серы, % 2	Сера и сернистые соединения, % 3					
		сероводород 4	элементарная сера 5	меркаптаны 6	дисульфиды 7	сульфиды 8	остаточная сера 9
10 Ишимбаевская	0,92	38	5,1	6,1	2,2	18,5	9,1
11 Туймазинская (угленосная свита)	0,45	15,7	3,0	11,2	7,1	5,3	57,7
12 Туймазинская (девонская) . .	0,86	10,4	3,4	22,1	9,5	36	18,6
13 Чусовская	0,396	7,3	4,3	15,3	0,52	32,6	39,8
14 Бугурусланская	0,02	2,3	3,7	5,7	17,6	22,6	48,1

1) Petroleum; 2) sulfur content, %; 3) sulfur and sulfur compounds, %; 4) hydrogen sulfide; 5) elementary sulfur; 6) mercaptans; 7) disulfides; 8) sulfides; 9) residual sulfur; 10) Ishimbay; 11) Tuymazy (Carboniferous strata); 12) Tuymazy (Devonian); 13) Chusovoy; 14) Buguruslan.

of the petroleum.

The group composition of the kerosene fractions of petroleums from various deposits is presented in Table 31, while the group composition of the fractions boiling over below 200° is presented in Table 32. The content of aromatic hydrocarbons, in the majority of the kerosene fractions, does not attain 20% and only rarely exceeds 25%.

The characteristic of the kerosene distillates of the petroleums is presented in Table 33. In the petroleums of the Second Baku, the sulfur content is quite substantial and exceeds the conventional norms for reaction fuels.

For turbojet-engine fuels, sulfur compounds represent some danger, primarily from the point of view of the corrosion of the fuel-feed system which consists of component parts made of nonferrous metals. With a high sulfur content in the fuel, and particularly in the case of active sulfur compounds (mercaptans) this equipment may break down.

Consequently, the content of sulfur in a reaction fuel and, in particular, the nature of the sulfur compounds are of great importance.

Tables 34 and 35 present the group compositions of sulfur compounds in isolated petroleum fractions and crude petroleums.

The most aggressive portion of the petroleum sulfur compounds are the mercaptans and elementary sulfur. Hydrogen sulfide, which is itself quite aggressive, is easily flushed out through alkali rinsing.

The composition of the sulfur compounds of the petroleums includes: elementary sulfur S, mercaptans RSH, the sulfides of the aliphatic series R-S-R and of the aromatic series Ar-S-Ar, disulfides R-S-S-R, cyclical sulfides $(CH_2)_nS$, thiophenes, thiophanes, and other more complex cyclical compounds.

The sulfides isolated from the petroleum represent a mixture of cyclical sulfides with five and six members in the cycle, among which

TABLE 35

Group Composition of Sulfur Compounds in Kerosene Fractions (200-300°)

1 Нефть	Содержание серы, %	3 Состав сернистых соединений, %					
	2	4 сероводород	5 элементарная сера	6 меркаптаны	7 дисульфиды	8 сульфиды	9 остаточная сера
10 Ишимбаевская	2,20	21,9	0,9	84	7,3	11,8	50,4
12 Шорсинская	0,62	8,90	5,6	6,4	2,6	6,0	71,6
13 Туймазинская (девонская) .	0,753	—	4,2	—	0,029	37,4	54,6
14 Бугурусланская	1,77	2,8	1,1	2,20	11,3	1,1	81,5
15 Ставропольская	0,957	0,410	2,40	0,522	1,56	30,63	64,67

1) Petroleum; 2) sulfur content, %; 3) composition of sulfur compounds, %; 4) hydrogen sulfide; 5) elementary sulfur; 6) mercaptans; 7) disulfides; 8) sulfides; 9) residual sulfur; 10) Ishimbay; 11) Shor-Su; 12) Tuymazy (Devonian); 13) Buguruslan; 14) Stavropol'.

TABLE 36

Sulfur Compounds in the Kerosene of Iranian Petroleum [4]

1 Соединение	2 Т. кип., °C	3 Соединение	4 Т. кип., °C
5 2-Метилтиоциклопентан . . .	132	14 2-Этил-5-метилтиоциклопентан	173
6 3-Метилтиоциклопентан . . .	137	15 2,3,4-Триметилтиофен	175—178
7 Тиоциклогексан	141	16 3-Этил-2,4-диметилтиофен . .	187—191
8 2,4-Диметилтиоциклопентан .	148	17 8-Тиобицикло-(3,2,1)-октан .	187—191
9 2-Метилтиоциклогексан . . .	153	18 4-Этил-2,3-диметилтиофен . .	193
10 2,3,5-Триметилтиоциклопентан	156	19 2,3,4,5-Тетраметилтиофен . .	—
11 3-Этилтиоциклопентан	156	20 1-Тиогидриндан	209—210
12 3,4-Диметилтиоциклогексан	164	21 Бициклические сульфиды . .	210—212
13 2,4,4-Триметилтиоциклопентан	171	22 Тетразамещенные тиофены .	213—227

1) Compound; 2) boiling point, °C; 3) compound; 4) boiling point, °C; 5) 2-methylthiocyclopentane; 6) 3-methylthiocyclopentane; 7) thiocyclohexane; 8) 2,4-dimethylthiocyclopentane; 9) 2-methylthiocyclohexane; 10) 2,3,5-trimethylthiocyclopentane; 11) 3-ethylthiocyclopentane; 12) 3,4-dimethylthiocyclohexane; 13) 2,4,4-trimethylthiocyclopentane; 14) 2-ethyl-5-methylthiocyclopentane; 15) 2,3,4-trimethylthiophene; 16) 3-ethyl-2,4-dimethylthiophene; 17) 8-thiobicyclo-(3,2,1)-octane; 18) 4-ethyl-2,3-dimethylthiophene; 19) 2,3,4,5-tetramethylthiophene; 20) 1-thiohydrindane; 21) bicyclic sulfides; 22) tetrasubstituted thiophenes.

we find thiocyclopentane, thiocyclohexane, and their homologs. Spectral investigations indicate the presence of mono-, di-, and tricyclical sulfides in the sulfur compounds of the petroleums.

The homologous series of cyclical sulfides having the general formula $(C_nH_{2n})S$ includes members ranging from C_4H_8S (boiling point, 140°) to $C_{18}H_{36}S$ (boiling point, $290-295^o$).

In the gasoline fractions from direct distillation, mercaptans with the radicals C_4-C_6 predominate, and this can be illustrated by the following data [3]:

	Boiling point, ^oC	Content, in %, in gasoline
CH_3SH	20	4
C_2H_5SH	39	6
C_3H_7SH	68	13
C_4H_9SH	98	19
iso-$C_5H_{11}SH$	116-118	18
$C_6H_{13}SH$	142	40

Moreover, homologs from methyl- to hexyl-sulfide exist among the sulfides, as well as more complex compounds of this series.

Thiophene, 2- and 3-methylthiophenes, 2- and 3-ethylthiophenes, 2,3- and 3,4-dimethylthiophenes have been found in the petroleums and the products of their heat treatment.

Cyclical and polycyclical sulfides (Table 36) have been found in the kerosene of Iranian petroleum.

In the 132° fraction, in addition to the cyclical sulfides, there are 50% aliphatic sulfides; however, in the $156-164^o$ fractions the content of these does not exceed 7-9%, and they are completely absent in the higher fractions. Polycyclical sulfides in quantities of 20-40% (of the total sulfur content) are contained in the $193-228^o$ fractions and in quantities of 40-60% in the $228-249^o$ fractions.

2. Composition of Fuel Fractions from the Products of the Heat Treatment of Petroleum and Solid Fuels

a) Products of cracking and pyrolysis

Cracking products serve as an additional source of reaction fuels. For example, 26-30% gasoline and 10-12% kerosene fractions are obtained in the thermal cracking of petroleum residue. The utilization of the

TABLE 37

Group Composition of Gasolines and Kerosenes Produced by Thermal and Catalytic Cracking

1 Продукт	Пределы кипения, °C 2	Групповой состав, % 3				
		непре-дельные 4	аромати-ческие 5	нафтено-вые 6	изопара-финовые 7	нормаль-ные пара-финовые 8
9 Крекинг-бензин	60—200	26,5	14,7	9,4	53,3	
10 Крекинг-керосин	100—240	17	24,4	22,8	23,4	12,4
»	95—298	19,4	23,0	28,6	60	
11 Крекинг-лигроиновая фракция каталитического крекинга	165—203	4	—	—	—	—
12 Крекинг-бензин каталитического крекинга	—	0,3	28,40	9—13	46—55	
13 Газойль каталитического крекинга	200—300	9,3	21,7	27,6	23,4	20

1) Product; 2) boiling range, °C; 3) group composition, %; 4) unsaturated; 5) aromatic; 6) naphthenic; 7) isoparaffinic; 8) normal paraffinic; 9) cracking gasoline; 10) cracking kerosene; 11) cracking-ligroin fraction of catalytic cracking; 12) cracking gasoline from catalytic cracking; 13) catalytic-cracking gas oil.

gasoline-kerosene cracking distillate makes it possible to expand the potential supply of reaction fuels. The catalytic-cracking gas-oil fractions used for this purpose, exhibiting a boiling range from 200 to 300°, would also be of some interest.

Thermal-cracking gasoline and kerosene fractions differ from the similar products of direct distillation primarily in the content of olefinic hydrocarbons. Table 37 presents the group composition of the thermal-cracking kerosenes and gasolines.

At the same time, the unsaturated compounds of the cracking dis-

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TABLE 38

Composition of Cracking-Kerosene
Fractions [7]

[1] Показатели	[2] Фракции, °C		
	95—200	200—250	250—300
[3] Иодное число	51,8	28,7	24,3
[4] Молекулярный вес	126	152	178
[5] Групповой состав, %			
[6] непредельные	25,6	17,1	17,0
[7] ароматические	6,3	20,6	31,1
[8] нафтеновые	27,1	27,4	30,0
[9] парафиновые	40,8	34,9	21,9
[10] Состав олефинов, %			
[11] циклические	2,4	—	2,4
[12] алифатические	4,7	1,2	—
[13] ароматические	19	16	15

1) Indicator; 2) fractions, $^{\circ}$C; 3)
iodine number; 4) molecular weight;
5) group composition, %; 6) unsat-
urated; 7) aromatic; 8) naphthenic;
9) paraffinic; 10) composition of
olefins, %; 11) cyclical; 12) ali-
phatic; 13) aromatic.

tillates, in terms of their structure in the basic mass, cannot be
identical to the olefins of the aliphatic series.

For example, V.S. Gutyrya and his co-workers [5], established the
presence of unsaturated hydrocarbons of cyclical structure in the
cracking- and reforming-gasolines, in addition to the aliphatic ole-
fins. A.V. Topchiyev and I.A. Musayev et al. [6] demonstrated that the
olefins of the aromatic series are contained in the cracking gasolines.

G.M. Mamedaliyev and F.D. Rzayeva [7], in investigating the com-
position of cracking kerosenes, detected aromatic hydrocarbons with an
olefin bond in the side chain. The composition of the cracking kero-
sene, according to the data from these authors, is presented in Table
38.

By means of the method of selective hydrogenation it has been pos-
sible to demonstrate that the basic mass of the unsaturated cracking-
kerosene hydrocarbons consists of the olefins of the aromatic series,

since the hydrogenation products contain primarily aromatic hydrocarbons. For example, in the 200-250 and 250-300° fractions, prior to hydrogenation, there were 17% olefins and, respectively, 20 and 31% aromatic hydrocarbons; after the complete hydrogenation of the olefins, the content of aromatic hydrocarbons increased to 36 and 46%, respectively.

Consideration of the nature of the olefins in the products of the thermal processing of the petroleum is of great significance in evaluating the reaction capacity and stability of the olefins.

From the standpoint of expanding the available supply of reaction fuels, it would be expedient to include the kerosene fractions of thermal and catalytic cracking into the reaction fuels.

The pyrolysis products (at temperatures between 600 and 700°) of the kerosene and similar distillates of petroleum may be regarded as possible raw material for the derivation of reaction fuels, if we take into consideration that the unsaturated hydrocarbons exhibit high reaction capacity with respect to nitric acid.

In the pyrolysis of kerosene, we obtain tar which is distilled into three basic fractions:

Oil	Specific weight
Light (to 170-190°)................	0.84-0.87
Medium (190-240°)................	0.900
Scrubber (240-300°)...............	0.950

Benzene, toluene, xylene, and unsaturated hydrocarbons are concentrated in light oil. This oil is rectified and the following are separated: the head fraction (below 73°), benzene (73-83°), toluene (108-113°), and xylenes (122-150°). The aromatic hydrocarbons separated in this case contain an additional substantial quantity of unsaturated compounds which are then removed by means of sulfuric-acid rinsing.

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TABLE 39

Chemical Composition of the Benzene-Head
Fraction, Boiling over below 50°

1 Углеводород	2 Формула	3 T. кип., °C	4 Количе-ство, %
5 2-Метилбутен-2	$CH_3 - C = CH - CH_3$ $\mid$ CH_3	38,4	} 17
6 2-Метилбутен-1	$CH_3 - CH_3 - C = CH_2$ $\mid$ CH_3	31	
7 Пентен-1	$CH_3=CH-CH_2-CH_2-CH_3$	40	} 42
8 Пентен-2	$CH_3-CH=CH-CH_3-CH_3$	38	
9 Циклопентадиен	$\begin{matrix} HC\!=\!=\!=\!CH \\ \mid \qquad\qquad \rangle CH_2 \\ HC\!=\!=\!=\!CH \end{matrix}$	41—42	5—6
10 Пентадиен-1,3	$CH_3=CH-CH=CH-CH_3$	42	3—7
11 2-Метилбутадиен-1,3 ...	$H_3C=C-HC=CH_3$ $\mid$ CH_3	34	10—12

1) Hydrocarbon; 2) formula; 3) boiling point,
°C; 4) quantity, in %; 5) 2-methylbutene-2;
6) 2-methylbutene-1; 7) pentene-1; 8) pen-
tene-2; 9) cyclopentadiene; 10) pentadiene-
1,3; 11) 2-methylbutadiene-1,3.

TABLE 40

Characteristics of Remaining Benzene-Head
and Light Oil Fractions

1 Продукт	2 Н. к., °C	3 К. к., °C	4 Мол. вес	5 Бромное число	6 Углеводороды
7 Бензольная головка	34	60	76	250	C_6
	60	75	84	168	$C_6—C_6$
	75	87	90	75	$C_6—C_7$
8 Легкое масло	60	87	92	140	C_7
	87	100	112	115	C_9
	100	140	132	71	C_{10}
	140	190	153	32	$C_{11}—C_{12}$

1) Product; 2) start of boiling, °C; 3) end
of boiling, °C; 4) molecular weight; 5) bro-
mine number; 6) hydrocarbon; 7) benzene head;
8) light oil.

After the separation of the benzene and toluene fractions, there
remains a substantial quantity of intermediate byproduct fractions
rich in aromatic hydrocarbons. In the wastes there remain fractions
which, when mixed in appropriate ratios, yield a gasoline which exhib-

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its high anti-knock properties. The latter is added to the direct-distillation gasoline in order to increase its anti-knock stability. By changing the pyrolysis regime, the gasoline may be obtained not as a byproduct but as the main product of the petroleum pyrolysis. However, the rinsing of the pyro-gasoline with sulfuric acid involves great losses, since a substantial quantity of the unsaturated hydrocarbon is lost in this case.

When the pyro-gasoline is used as a propellant component in liquid rocket engines, the removal of the unsaturated hydrocarbons may prove to be undesirable. The low stability of such a propellant, capable of introducing complications, may be increased by means of inhibitors.

The first runnings (head fraction) of light oil contain some 60% unsaturated hydrocarbons consisting of amylenes and hexylenes, and a smaller quantity of diene hydrocarbons. There is some 40% benzene in this fraction.

The benzene head is capable of auto-oxidation in air, i.e., of combining slowly with oxygen. This indicates its high reaction capacity. The chemical composition of the benzene head is extremely complex and has not as yet been fully clarified. The amylene fraction of the benzene head, boiling over below 50°, has the composition shown in Table 39.

The composition of the benzene head and light oil is characterized by the following data:

The Benzene Head

Fractional composition
 start of boiling, ^{o}C............... 34
 50%, distilled below............... 75°
 end of boiling, ^{o}C................ 87
Density................................. 0.80

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Bromine number......................... 152

Molecular weight....................... 82

Contains, %

     unsaturated....................... 75-80

     amylenes and pentadienes.......... 52

     hexylenes......................... 18

     benzene........................... 25-30

Light Oil

Fractional composition

     start of boiling, ^{o}C............. 60

     50% distilled below............... 110°

     end of boiling, ^{o}C............... 190

Density................................ 0.84

Bromine number......................... 98

Content of unsaturated hydrocarbons, %.. · 90

On the whole, the benzene head and the light oil, with respect to fractions, have the characteristics shown in Table 40.

b) Polymer-gasolines

The polymer gasolines, obtained by the polymerization of gaseous olefins (propylene, butylenes) and partially by the polymerization of the olefins of the head cracking-gasoline fractions (amylenes), may be

TABLE 41

Polymer-Gasoline Characteristics

1 Процесс полимеризации	2 Фракционный состав, °C						Плотность	Бром-ное число
3	н. к.	30%	50%	70%	90% 4 к. к.		5	6
7 Полимеризация пропилена .	36	120	135	153	190	222	—	125
8 Полимеризация бутиленов (октиленовая фракция) ..	98	107	108	110	111	—	0,72	—
9 Общая полимеризация олефинов C₃ — C₄	32	93	106	126	164	200	0,71	127

1) Polymerization process; 2) fractional composition, ^{o}C; 3) start of boiling; 4) end of boiling; 5) density; 6) bromine number; 7) polymerization of propylene; 8) polymerization of butylenes (octylene fraction); 9) general polymerization of olefins C_3-C_4.

TABLE 42

Hydrocarbon Composition of the Polymers of Propylene, Butylenes, and Amylenes [8]

1 Исходные углеводороды	2 Димеры	3 Тримеры	4 Тетрамеры и пентамеры
5 Пропилен	2-Метилпентен-1 12 4-Метилпентен-1 13 2,3-Диметилбутен-1 14 2,3-Диметилбутен-2 15 2-Метилпентен-2 16 3-Метилпентен-2 17	3-Этил-4,4-диметилпентен-2 31 3,4,5-Триметилгексен-4 32 Вероятно, присутствуют 3,4-диметилгептен-3 и 2,4-диметилгептен-3 33	—
6 Изобутилен + пропилен	4,4-Диметилпентен-1 18 2,3-Диметилпентен-2 19	—	—
7 Псевдобутилен (бутен-2)	3,4-Диметилгексен-2 20	—	—
8 Изобутилен	2,4,4-Триметилпентен-1 21 2,4,4-Триметилпентен-2 22, 23	2,4,4,6,6-Пентаметилгептен-3 34 2,4,4,6,6-Пентаметилгептен-1 35	2,4,4,6,6,8,8-Гептаметилнонен-1 и немного 2,2,6,6-тетраметил-4-неопентилгептена-3 (в пентамере содержатся только формы с двойной связью в конце молекулы) 38
9. Изобутилен + н. бутилен	3,4,4-Триметилпентен-2 2,3,4-Триметилпентен 24, 25	2,4,4,6,6-Пентаметилгептен-2 36	
10 Изобутилен + изоамилен	2,3,5-Триметилгексен-2 2,2-Диметил-3-этилпентен-3 26	1,1-Динеопентилэтилен 37	—
11 Изоамилен	2,3,4,4-Тетраметилгексен-2 27 3,5,5-Триметилгептен-3 28 3,5,5-Триметилгептен-2 29 3,4,5,5-Тетраметилгексен-2 30	—	—

1) Initial hydrocarbon; 2) dimers; 3) trimers; 4) tetramers and pentamers; 5) propylene; 6) isobutylene + propylene; 7) pseudobutylene (butene-2); 8) isobutylene; 9) isobutylene + low butylene; 10) isobutylene + isoamylene; 11) isoamylene; 12) 2-methylpentene-1; 13) 4-methylpentene-1; 14) 2,3-dimethylbutene-1; 15) 2,3-dimethylbutene-2; 16) 2-methylpentene-2; 17) 3-methylpentene-2; 18) 4,4-dimethylpentene-1; 19) 2,3-dimethylpentene-2; 20) 3,4-dimethylhexene-2; 21) 2,4,4-trimethylpentene-1; 22) 2,4,4-trimethylpentene-2; 23) 3,4,4-trimethylpentene-2; 24) 2,3,4-trimethylpentene; 25) 2,3,5-trimethylhexene-2; 26) 2,2-dimethyl-3-ethylpentene-3; 27) 2,3,4,4-tetramethylhexene-2; 28) 3,5,5-trimethylheptene-3; 29) 3,5,5-trimethylheptene-2; 30) 3,4,5,5-tetramethylhexene-2; 31) 3-ethyl-4,4-dimethylpentene-2; 32) 3,4,5-trimethylhexene-4; 33) probably, there are 3,4-dimethylheptene-3 and 2,4-dimethylheptene-3 present; 34) 2,4,4,6,6-pentamethylheptene-3; 35) 2,4,4,6,6-pentamethylheptene-1; 36) 2,4,4,6,6-pentamethylheptene-2; 37) 1,1-dineopentylethylene; 38) 2,4,4,6,6,8,8-heptamethylnonene-1 and some 2,2,6,6-tetramethyl-4-neopentylheptene-3 (the pentamer contains only shapes with a double bond at the end of the molecule).

regarded as a source for increasing the available supply of reaction

fuels. The composition of industrial polymers is a function of the type

of raw material used and of the process designation.

Table 41 presents the characteristics of industrial polymer-gasolines.

The polymer gasoline of the total polymerization (olefins C_3H_6 + C_4H_8) is not subject to hydrogenation, since after hydrogenation the octane number of the gasoline diminishes as a result of the fact that the polymer contains olefins that have little branching.

The polymer gasoline of the total polymerization to 93-95% consists of olefins with a small admixture of other hydrocarbons (0.5-1% aromatic hydrocarbons and 3.5-6% paraffins and naphthenes), which are formed as a result of the hydro-dehydropolymerization.

The polymerization of propylene by phosphoric acid at 160° and 10 atm makes it possible to obtain a polymer of the following composition: C_6H_{12}, 5%; C_9H_{18}, 50%; $C_{12}H_{24}$, 25%; $>C_{12}$, 20%.

At higher temperatures and pressures, the process can be directed toward the primary formation of dodecylene which is used as a semifinished product for the production of synthetic detergents.

We can reach some conclusion as to the composition of the polymers of propylene, butylenes, and isoamylenes, on the basis of data from a number of investigators, said data presented in Table 42.

The polymer gasolines cannot be regarded as basic components of reaction fuels; however, they may be included in the over-all supplies of reaction fuels.

c) Products of the treatment of solid fuel

The products which result from the treatment of shales and coals during the semicoking process may be regarded as possible components of reaction fuels.

The semicoking process of shales, lignite, and coal is carried out at a temperature below $550-600^\circ$, as a result of which up to 15-20%

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tar is produced from the shales, and 10-15% tar is produced by the semicoking of lignite and coal, with approximately 50% of the tar boiling over, during distillation, below 350°.

The chemical composition of the tar is extremely complex. There are hydrocarbons, oxygen-bearing sulfur and nitrogen-bearing compounds in the composition of the tar. The total content of oxygen-bearing compounds reaches 50%, of which up to 20% is made up by phenols. The sulfur-compound content ranges between 10-20%, and the content of nitrogen-bearing compounds does not exceed 2%. Approximately 30-35% of the shale tar is made up of hydrocarbons: unsaturated, paraffinic, naphthenic, and aromatic. The phenols are contained in the fractions that boil over primarily above 300°; the hydrocarbons predominate in those fractions boiling over below 300°.

The unsaturated hydrocarbons predominate in the hydrocarbon fraction (up to 60-65%) of the shale tar. There are also diolefins in small quantities. The content of naphthenic and aromatic hydrocarbons, together, does not exceed 16-20%.

The chemical composition of the middle fraction of the shale tar, according to Ball's data [9] is given in Table 43.

The shale-tar fraction which boils between 90 and 300° contains up to 40% olefins and cycloolefins.

In the hydrogenation of petroleum residues, lignite, and coal under a pressure of 300-600 atm (the required pressure is selected on the basis of the type and composition of the raw material), and at a temperature of $450-500^\circ$, the yield of liquid fuels amounts to 60-70%.

Here we will obtain high-quality distillates which can be used as the raw material for the derivation of fuels for air-reaction engines, and the only problem here is the extent to which it is economically feasible to produce this fuel by means of hydrogenation.

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3. Structure and Physicochemical Properties of the Hydrocarbons of Fuel Fractions [10,11]

The hydrocarbons which enter into the compositions of the gaso-line, and in particular, of the kerosene fractions of the petroleum determine, in first order, the low-temperature properties of the fuels and the fuel yield from the petroleum. For example, the pour point of a reaction fuel to a great extent is determined by the content of par-affinic hydrocarbons which, given an identical number of carbon atoms, in comparison with the naphthenic and aromatic hydrocarbons exhibit the highest melting points.

Thus, for example, the C_{15} hydrocarbons have the following melt-ing points:

$$^{o}C$$

n. Pentadecane $C_{15}H_{32}$....................... +9.8
Cyclopentyldecane $C_{15}H_{30}$.................... −23.5
1-Methyl-4-octylbenzene $C_{15}H_{24}$............. −26.5

However, the structure of the hydrocarbons within the limits of one and the same homologous series and molecular formula has a signifi-cant effect on the melting point.

The paraffinic hydrocarbons of normal- and iso-structure differ markedly between one another in terms of melting point (Table 44).

The isoparaffins, in comparison with the paraffins of normal structure, exhibit extremely low melting points. However, exceptions to this rule do occur, when the structure of the molecule of the iso-structure attains maximum symmetry.

For example, the melting point of n. octane is $−56.8^{o}$; of 3-meth-ylheptane, $−120.5^{o}$; of tetramethylbutane, which is a solid hydrocarbon having a melting point of $+100.6^{o}$.

Table 45 presents a summary of the changes in melting points for paraffinic hydrocarbons as a function of the number of carbon atoms in

TABLE 43

Hydrocarbon Composition of Middle Fraction (90-300°) of Shale Tar [9]

1 Парафины	%	2 Нафтены	%	3 Ароматические углеводороды	%	4 Олефины	%	5 Циклоолефины	%
6 н.Гексан	0,1	17 Циклогексан	0,03	24 Бензол	0,2	37 н.Нонен	4,2	41 Циклогексен	0,1
7 Метилгексан	0,2	18 Метилциклогексан	0,03	25 Толуол	1,1	38 Изо-Децен	1,9	42 Циклогептен	0,5
8 н.Гептан	0,2	19 Этилциклопентан	0,04	26 Этилбензол	0,3	39 Додецен	4,3	43 Циклооктен	1,4
9 Диметилгексан	0,3	20 1,2,4-Триметилциклопентан	0,10	27 о-Ксилол	0,7	40 Остаток	13,0	44 Циклононен	3,2
10 Метилгептан	0,2	21 Прочие C_8	—	28 м-Ксилол	1,6	47 И т о г о	23,4	45 Циклодецен	
11 н.Октан	1,6	22 Нафтены C_9	0,7	29 о-Ксилол	0,9			46 Остаток	1,6
12 Диметилгептаны	0,6	C_{10}	2,1	30 1-Метил-3-этилбензол	0,8			Остаток	8,3
13 Метилоктаны	0,5	23 Остаток	1,6	31 1-Метил-4-этилбензол	0,4			47 И т о г о	16,1
14 Метилнонаны и другие изододеканы	2,2	47 И т о г о	8,8	32 1-Метил-2-этилбензол / 1,3,5-Триметилбензол	0,9				
15 н.Декан	4,1			34 1,2,4-Триметилбензол	1,5				
16 Остаток	9,3			35 1-Метил-2-изопропилбензол	—				
47 И т о г о	22,7			36 1-Метил-3-изопропилбензол	1,8				
				47 И т о г о	10,2				

1) Paraffin; 2) naphthenes; 3) aromatic hydrocarbons; 4) olefins; 5) cycloolefins; 6) n. Hexane; 7) Methylhexane; 8) n. Heptane; 9) Dimethylhexane; 10) Methylheptane; 11) n. Octane; 12) Dimethylheptanes; 13) Methyloctanes; 14) Methylnonanes and other isodecanes; 15) n. Decane; 16) residue; 17) Cyclohexane; 18) Methylcyclohexane; 19) Ethylcyclopentane; 20) 1,2,4-Trimethylcyclopentane; 21) other C_8; 22) Naphthenes; 23) residues; 24) Benzene; 25) Toluene; 26) Ethylbenzene; 27) p-Xylene; 28) m-Xylene; 29) o-Xylene; 30) 1-Methyl-3-ethylbenzene; 31) 1-Methyl-4-ethylbenzene; 32) 1-Methyl-2-ethylbenzene; 33) 1,3,5-Trimethylbenzene; 34) 1,2,4-Trimethylbenzene; 35) 1-Methyl-2-isopropylbenzene; 36) 1-Methyl-3-isopropylbenzene; 37) residues; 38) Nonene; 39) isodecene; 40) Dodecene; 41) Cyclohexene; 42) Cycloheptene; 43) Cyclooctene; 44) Cyclononene; 45) Cyclodecene; 46) residues; 47) total.

TABLE 44

Melting Point of Paraffinic Hydrocarbons of Normal- and Iso-Structure

1 Углеводород	2 т. пл., °C	3 т. кип., °C
4 н. Декан	— 20,6	174,1
5 2-Метилнонан	— 74,6	167,0
6 3-Метилнонан	— 84,8	167,8
7 5-Метилнонан	— 86,4	165,1
8 2,7-Диметилоктан	— 54,6	159,8
9 2,2,6-Триметилгептан	—105	148,9
10 н. Додекан	— 9,6	216,2
11 3-Этилдодекан	— 71	201,5
12 4,5-Диэтилоктан	— 70	192—194
13 н. Тетрадекан	+ 5,5	253,6
14 2,11-Диметилдодекан	— 8,5	244
15 4,5-Дипропилоктан	<— 80	220
16 н. Гексадекан	+ 18,1	287
17 3-Метилпентадекан	— 22,3	267
18 5,7-Диэтилдодекан	<— 80	254
19 7,8-Диметилтетрадекан . . .	— 70	267—269
20 н. Октадекан	+ 28,1	317,5
21 9-Метилгептадекан	— 8	—
22 3,12-Диэтилтетрадекан . . .	<— 30	—
23 7,8-Диэтилтетрадекан . . .	— 36	—

1) Hydrocarbon; 2) melting point, °C; 3) boiling point, °C;
4) n. Decane; 5) 2-Methylnonane; 6) 3-Methylnonane; 7) 5-Methylnonane; 8) 2,7-Dimethyloctane; 9) 2,2,6-Trimethylheptane; 10) n. Dodecane; 11) 3-Ethyldodecane; 12) 4,5-Diethyloctane; 13) n. Tetradecane; 14) 2,11-Dimethyldodecane; 15) 4,5-Dipropyloctane; 16) n. Hexadecane; 17) 3-Methylpentadecane; 18) 5,7-Diethyldodecane; 19) 7,8-Dimethyltetradecane; 20) n. Octadecane; 21) 9-Methylheptadecane; 22) 3,12-Diethyltetradecane; 23) 7,8-Diethyltetradecane.

TABLE 45

Melting Point of Paraffinic Hydrocarbons as a Function of the Number of Side Chains

1 Число атомов углерода в молекуле	2 Т. пл., °C 3 при числе боковых цепей				
	0	1	2	3	4
9	—53,7	—80—115	—	—	до — 120
10	—29,7	—74—98	—53	—105	—
11	—25,6	—93	—	—	—
12	— 9,6	—70	—	—	—
13	— 6,2	—65	—	—	—

1) Number of carbon atoms in molecule; 2) melting point, °C; 3) number of side chains.

the molecules and the number of side chains.

Table 46 presents the melting points of paraffins and olefins of normal structure. Given an equal number of carbon atoms, the olefins have lower melting points than the paraffins.

The content of paraffinic hydrocarbons of normal- and iso-structure in kerosene fractions of various petroleums is presented in Table 47.

Since the olefins of isostructure have lower melting points, the melting point of the olefins diminishes after their isomerization. For example, in the case of isomerization, by activated aluminum oxides, of dodecene-1 ($C_{12}H_{24}$), tridecene ($C_{13}H_{26}$), and hexadecene-1 ($C_{16}H_{32}$), at 300°, the following results were obtained (Table 48).

The isomerization of normal paraffins at 400° over a sulfur catalyst results in a reduction of the pour point of the isomerizate, depending on the extent of isomerization (Table 49).

The melting point of naphthenic hydrocarbons with long side chains in all cases is lower than the melting point of normal paraffinic hydrocarbons and, therefore, the naphthenic hydrocarbons are more desirable as components in a reaction fuel (Table 50).

The content of the naphthalene homologs in the kerosene fractions of the petroleums being investigated amounts to approximately 3% of all the aromatic hydrocarbons.

The benzene homologs, having equal numbers of atoms in the side chains, can exhibit the greatest variety of melting points. For example, n. butylbenzene melts at -87.5^O; 1,2,3,5-tetramethylbenzene melts at -23.8^O; and 1,2,4,5-tetramethylbenzene is solid and has a melting point of $+79^O$. Naphthalene is a solid; α-methylnaphthalene is a liquid which solidifies at -19°; β-methylnaphthalene is a solid, and 2,3- and 2,6-dimethylnapthalenes are also solids which melt at around 100°.

TABLE 46

Melting Point and Boiling Point
for Normal Paraffins and Nor-
mal Olefins

Углеводород 1	Т. пл., °C 2	Т. кип., °C 3
4 Декан	—29,6	174,1
5 Децен-1	—66,3	170,5
6 Додекан	— 9,6	216,2
7 Додецен-1	—33,6	213,3
8 Тетрадекан	+ 5,5	253,6
9 Тетрадецен-1	—12,0	246

1) Hydrocarbon; 2) melting
point, °C; 3) boiling point,
°C; 4) decane; 5) decene-1; 6)
dodecane; 7) dodecene-1; 8)
tetradecane; 9) tetradecene-1.

TABLE 47

Content and Composition of Paraffins in
Kerosenes

1 Керосин	2 Содержание, %		
	парафины 3	нормальные парафины 4	изопарафины 5
6 Туймазинский (девонский)	55,2	28,7	26,5
7 Карачухурский	50	13,0	37,6
8 Сураханский (легкой нефти)	14	0	14

1) Kerosene; 2) content, %; 3) paraffins;
4) normal paraffins; 5) isoparaffins; 6)
Tuymazy (Devonian); 7) Kara-Chukhur; 8)
Surakhany (from light petroleum).

TABLE 48

Reduction of Melting Point in the Isomerization of
Normal Olefins

1 Исходный углеводород	Выход изомеризата, % 2	3 Т. пл., °C		Показатель преломления изоалкена, n_D^{20} 6
		н. алкен 4	изоалкен 5	
7 Додецен-1	65	—38,6	—57	1,4233
8 Тридецен-1	65	—22,2	—58	1,4265
9 Гексадецен-1	50	+ 4	—30	1,4420

1) Initial hydrocarbon; 2) yield of isomerizate, %;
3) melting point, °C; 4) n. alkene; 5) isoalkene;
6) isoalkene refraction index, n_D^{20}; 7) dodecene-1;
8) tridecene-1; 9) hexadecene-1.

TABLE 49

Reduction of Melting Point after Isomerization of Mixture of Normal Paraffins $C_{12}H_{26}$-$C_{16}H_{34}$

1) Углеводороды	2) т. пл., °C	3) Плотность ρ_4^{20}	n_D^{20}	4) Бромное число	5) Выход, %
6) н. Парафины	—21	0,7716	1,4280	0	—
7) Изомеризат*.	—48	0,7700	1,4326	0	96
8) Изопарафины	—70	0,7710	1,4200	0	50

*Mixture of paraffins of normal- and isostructure.
1) Hydrocarbons; 2) melting point, °C; 3) density, ρ_4^{20}; 4) bromine number; 5) yield, %; 6) n. paraffins; 7) isomerizate*; 8) isoparaffins.

TABLE 50

Melting and Boiling Points for Naphthenic and Normal Paraffinic Hydrocarbons with the Same Number of Carbon Atoms

1) Число атомов углерода	2) Углеводород	3) т. пл., °C	4) т. кип., °C
C_9 — 5)	н. Нонан	— 53,5	150,7
C_9 — 6)	Бутилциклопентан	—107,9	156
C_{10} — 7)	н. Декан	— 29,6	174,1
C_{10} — 8)	Бутилциклогексан	— 74,4	180
C_{13} — 9)	н. Тридекан	— 6	235,5
C_{13} — 10)	Циклогексилгептан	— 41	—
C_{13} — 11)	Циклопентилоктан	— 44,5	—
C_{15} — 12)	Пентадекан	+ 9,8	2;0,6
C_{15} — 13)	Циклопентилдекан	— 23	—

1) Number of carbon atoms; 2) hydrocarbon; 3) melting point, °C; 4) boiling point, °C; 5) n. nonane; 6) butylcyclopentane; 7) n. decane; 8) butylcyclohexane; 9) n. tridecane; 10) cyclohexylheptane; 11) cyclopentyloctane; 12) pentadecane; 13) cyclopentyldecane.

Thus the source for the formation of crystals in a fuel at low temperatures may be the polymethylated benzenes and naphthalenes, in addition to the paraffins of normal structure. However, the content of the former in kerosenes is substantially less than of the latter.

Viscosity is a characteristic on which depends the pumpability of fuels at low temperatures.

TABLE 51

Viscosity of Hydrocarbons as Function of Their Structure

1 Углеводород	2 Ряд углеводородов	3 Формула	4 Т. кип., °C	5 Динамическая вязкость η_{20}, ccm
6 н. Гексан. 21	Парафины	C_6H_{14}	68,7	0,320
7 н. Октан	•	C_8H_{18}	125,6	0,540
8 4-Метилгептан	•	C_8H_{18}	117,1	0,470
9 Этилциклогексан 22	Нафтены	C_8H_{16}	131,7	0,895
10 м-Ксилол 23	Ароматические	C_8H_{10}	139,1	0,615
11 н. Декан 24	Парафины	$C_{10}H_{22}$	174,1	0,920
12 5-Метилнонан	•	$C_{10}H_{22}$	167,0	0,810
13 Децен-1 25	Олефины	$C_{10}H_{20}$	170,5	0,806
14 н. Бутилциклогексан . . . 26	Нафтены.	$C_{10}H_{30}$	180,9	1,290
15 н. Бутилбензол 27	Ароматические ·	$C_{10}H_{14}$	183,8	1,030
16 н. Пентадекан 28	Парафины	$C_{15}H_{32}$	270,6	2,860
17 2-Метилтетрадекан	•	$C_{15}H_{32}$	265,4	3,330
18 Пентадецен-1 29	Олефины	$C_{15}H_{30}$	258	2,500
19 Децилциклогексан 30	Нафтены	$C_{16}H_{32}$	—	5,010
20 н. Нонилбензол 31	Ароматические	$C_{15}H_{34}$	280—281	3,220

1) Hydrocarbon; 2) hydrocarbon series; 3) formula;
4) boiling point, °C; 5) dynamic viscosity, η_{20},
centistokes; 6) n. hexane; 7) n. octane; 8) 4-methylheptane; 9) ethylcyclohexane; 10) m-xylene;
11) n. decane; 12) 5-methylnonane; 13) decene-1;
14) n. butylcyclohexane; 15) n. butylbenzene; 16)
n. pentadecane; 17) 2-methyltetradecane; 18) penta-decene-1; 19) decylcyclohexane; 20) n. nonylben-zene; 21) paraffins; 22) naphthenes; 23) aromatic;
24) paraffins; 25) olefins; 26) naphthenes; 27)
aromatic; 28) paraffins; 29) olefins; 30) naph-thenes; 31) aromatic.

The viscosity of the hydrocarbons of the gasoline-kerosene fractions increases uniformly with an increase in molecular weight. Viscosity decreases in the series naphthenes-aromatic hydrocarbons-paraffins-olefins (Table 51).

The isoparaffins, branching very little, differ only slightly in terms of viscosity from the normal-structure paraffins.

The change in the viscosity of hydrocarbons of various homologous series, as a function of their boiling point, is presented in Fig. 51.

With an increase in fuel viscosity, the specific fuel consumption can increase as a result of the impairment of vaporization and mixture formation.
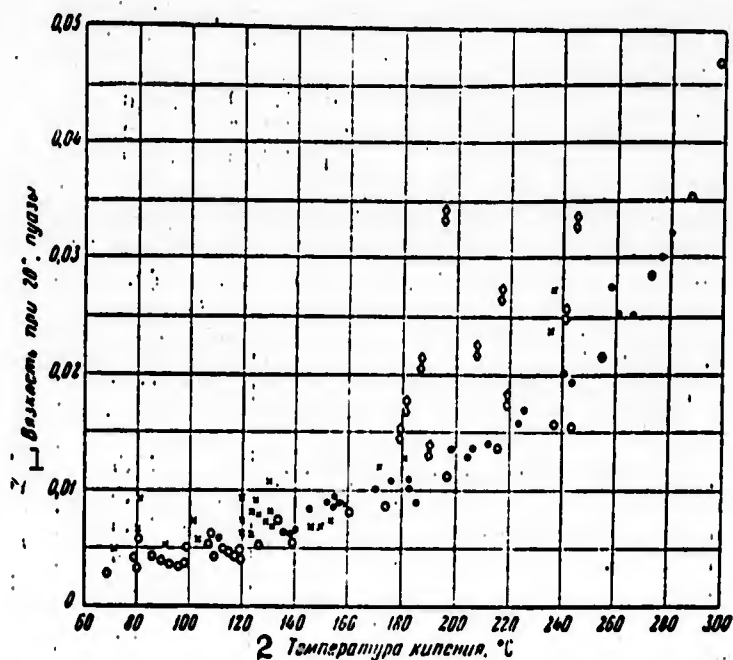
Fig. 51. Viscosity of hydrocarbons of various
homologous series as a function of the boiling
point. 0) Alkanes; x) cyclanes; ●) aromatic hydro-
carbons; ⅋) bicyclic hydrocarbons; 1) viscosity at
20°, poises; 2) boiling point, °C.
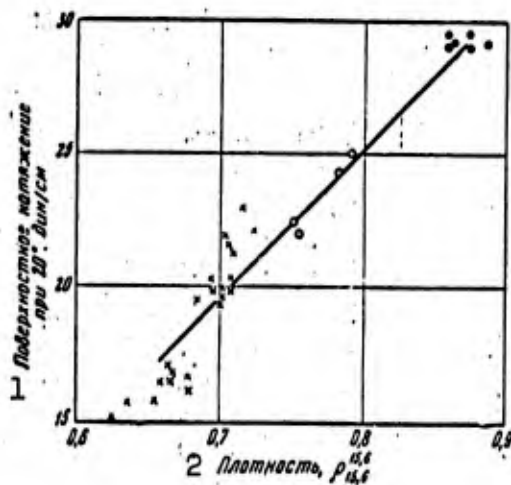
Fig. 52. Surface tension of
hydrocarbons of various series
as function of density. x) Al-
kanes; 0) cyclanes; ●) aromatic
hydrocarbons; 1) surface ten-
sion at 20°, dyn/cm; 2) den-
sity, $\rho_{15.6}^{15.6}$.

There is a direct relationship between the surface tension of the
fuel and the degree of fuel vaporization; therefore, this characteris-
tic of hydrocarbons should not be neglected. The least value of surface

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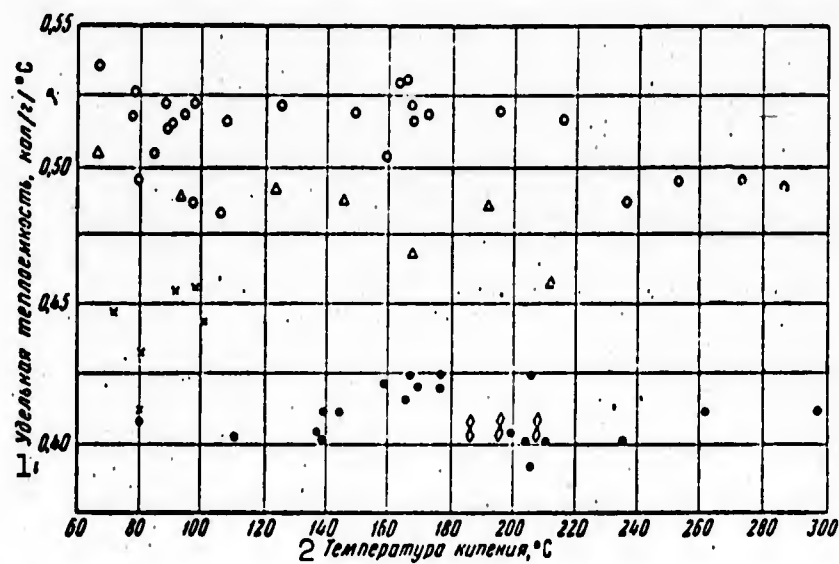
Fig. 53. Heat capacity of hydrocarbons of various series as a function of the boiling point. 0) Alkanes; Δ) alkenes; x) cyclanes; ●) aromatic hydrocarbons; ⚯) bicyclic hydrocarbons; 1) specific heat capacity, cal/g/°C; 2) boiling point, °C.
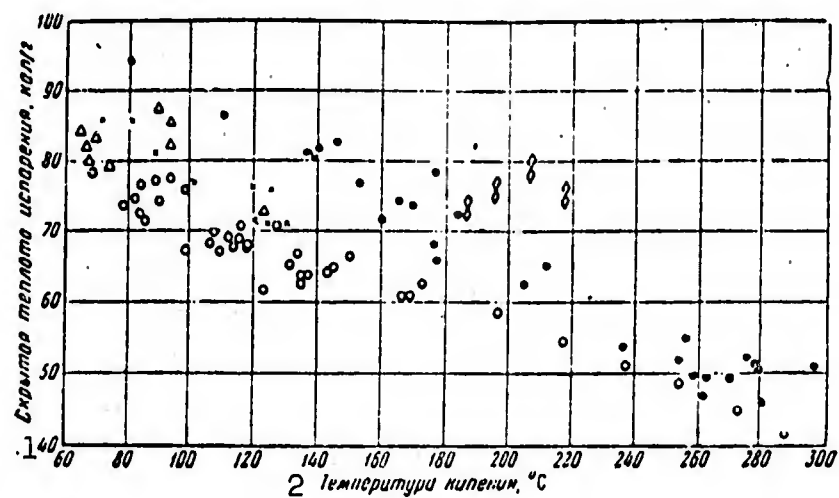
Fig. 54. Latent heat of vaporization of hydrocarbons of various series as function of boiling point. 0) Alkanes; Δ) alkenes; x) cyclanes; ●) aromatic hydrocarbons; ⚯) bicyclic hydrocarbons; 1) latent heat of vaporization, cal/g; 2) boiling point, °C.

tension is exhibited by paraffinic hydrocarbons: from 18 to 28 dyn/cm; the highest values are exhibited by aromatic hydrocarbons: from 28 to 32 dyn/cm; and the naphthenes occupy an intermediate position.

In general, the surface tension of fuel fractions of petroleum products, at 20°, lies between 15 and 40 dyn/cm. Figure 52 shows the
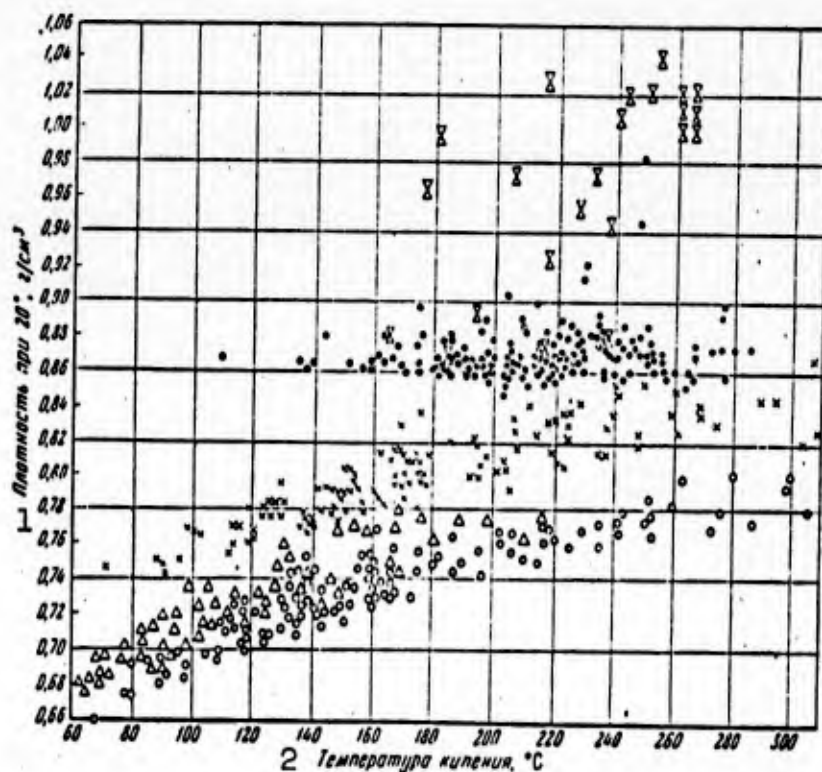
Fig. 55. Density of hydrocarbons as function of
boiling point. 0) Alkanes; Δ) alkenes; x) cyclanes;
●) aromatic hydrocarbons; ⚇) bicyclic hydrocar-
bons; 1) density at 20°, g/cm³; 2) boiling point, °C.

TABLE 52

Density of Hydrocarbons of Various
Series

1 Углеводород	Формула 2	Плотность ρ_4^{20} 3	Т. кип., °C 4
	C_{10}		
5 н. Декан	$C_{10}H_{22}$	0,7299	174
6 н. Децен	$C_{10}H_{20}$	0,7708	170,5
7 2-Циклогексилбутан . . .	$C_{10}H_{20}$	0,8131	179
8 Декалин (цис)	$C_{10}H_{18}$	0,8950	193,3
9 н. Бутилбензол	$C_{10}H_{14}$	0,8603	183,8
10 Нафталин	$C_{10}H_8$	1,145	217,9
	C_{12}		
11 н. Додекан	$C_{12}H_{26}$	0,7487	216,2
12 Додецен-1	$C_{12}H_{24}$	0,7584	213,3
13 3-Циклогексилгексан . . .	$C_{12}H_{24}$	0,8225	217
14 3-Фенилгексан	$C_{12}H_{18}$	0,8614	200—203
15 β-Этилнафталин	$C_{12}H_{12}$	1,002	251

1) Hydrocarbon; 2) formula; 3) density, ρ_4^{20}; 4) boiling
point, °C; 5) n. decane; 6) n. decene; 7) 2-cyclohexylbutane;
8) decalin (cis); 9) n. butylbenzene; 10) naphthalene; 11)
n. dodecane; 12) dodecene-1; 13) 3-cyclohexylhexane; 14) 3-
phenylhexane; 15) β-ethylnaphthalene.

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change in the surface tension of hydrocarbons of various series as a function of specific weight. This relationship can be given by the following formula: $\sigma = 51.5$, $d - 16.6$.

The surface tension of petroleum products having a specific weight between 0.71 (gasoline) and 0.81 (kerosene) changes at 20° from 20 to 27 dyn/cm.

With respect to the remaining properties of hydrocarbons, let us dwell in detail on the specific heat capacity and latent heat of vaporization, since these may prove to be of interest in connection with the problem of cooling an engine.

The specific heat capacity of hydrocarbons of various series is found approximately to range between 0.4 and 0.5 cal/g·deg. As can be seen in Fig. 53, the paraffins exhibit the greatest heat capacity. The hydrocarbons, rich in carbon, exhibit the least heat capacity.

The latent heat of vaporization of hydrocarbons boiling between $60-300^{\circ}$ is found approximately to range between 40 and 95 kcal/kg.

The lowest heat of vaporization is found with paraffinic hydrocarbons; and the greatest heat of vaporization is found with aromatic hydrocarbons (Fig. 54).

The density of hydrocarbons determines the density of the fuels, and this has an effect on the supply of fuel in the aircraft's tanks. The greater the density of the fuel, the more fuel can be carried, given equal tank capacity.

Table 52 presents the density of hydrocarbons of various series in the case of equal numbers of carbon atoms.

Cyclical hydrocarbons exhibit greater density in comparison with hydrocarbons having an open chain. The density of aromatic hydrocarbons is greater than the density of naphthenic hydrocarbons. The homologs of naphthalene exhibit particularly high density. For example,

for methyl- and ethylnaphthalenes, the density is close to unity.

In general, the density of hydrocarbons as a function of their boiling points can be presented in the form of a graph (Fig. 55). The density of the alkanes and alkenes within a range of boiling points from 60 to $300°$ increases from 0.68 to 0.80; in the case of monocyclical naphthenes it increases from 0.74 to 0.88; and in the case of aromatic hydrocarbons it increases from 0.86 to 0.90. Bicyclic aromatic hydrocarbons exhibit the highest density, i.e., from 0.95 to 1.04.

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Chapter 4

COMPOSITION AND HEATING VALUE OF JET FUELS

1. Definition of Heating Value and its Limits for Fuels

Heating value is one of the most important parameters characterizing the properties of a jet fuel. Attempts are made to use as fuel substances consisting of elements or compounds with the highest possible heating value. The term heating value or calorific value refers to the quantity of heat in calories that is liberated on combustion of a unit weight (1 kg) or volume (1 liter) of material in an oxygen or air atmosphere. Accordingly, two methods exist for expressing heating value: heating value per unit weight and heating value per unit volume.

The standard quantity is the unit-weight heating value. The concept of volume heating value is frequently employed as a supplementary characteristic for aviation fuels, since flight range depends on it to a certain degree.

Two values of the unit-weight heating value are distinguished: the upper and lower limits.

The upper-limit heating value is the quantity of heat liberated in complete combustion of a unit weight of fuel at a pressure of 760 mm Hg with the combustion products cooled to 25°. The upper-limit heating value is determined by burning the material in a bomb calorimeter in an oxygen atmosphere.

The lower-limit heating value is the quantity of heat liberated during complete combustion of a unit weight of fuel at a pressure of 760 mm Hg with the combustion products cooled to 25°, but without tak-

ing into account the heat of condensation of the water vapor formed during combustion of the fuel.

For a number of substances (such as Al, B, Be and their compounds) combustion of which results in formation of high-boiling oxides (e.g., Al_2O_3, B_2O_3, BeO) and, in certain cases, water vapor, the physical state of the combustion products (solid, liquid or gaseous) is also indicated in giving the heating-value figure.

Table 53 lists heating values per unit weight and volume for elements whose combustion is accompanied by liberation of a large quantity of heat as compared with the remaining elements of the periodic system.

The heating values of such elements as phosphorus, titanium, vanadium, calcium, zirconium, niobium, sodium and sulfur lie in the range from 2000 to 5660 kcal/kg. For the remaining elements of the periodic system, the heating value does not reach 2000 kcal/kg.

Hydrogen, combustion of which liberates 28,900 kcal/kg, has the highest heating value. The heating value of the hydrocarbons is the lower unit-weight heating-value limit beyond which it is evidently not advisable to go for air-breathing jet-engine fuels.

The heating values for hydrocarbons of the various series lie in the range from approximately 9500 to 10,500 kcal/kg and average about 10,000 kcal/kg.

Apart from hydrogen, only beryllium and boron surpass the hydrocarbon fuels as regards their unit-weight heating values; consequently, the selection of fuels with higher heating values is quite limited. Under ordinary conditions, however, hydrogen is a gas and has an excessively low density of 0.07 in liquid form at $-252.8°$; this excludes the provision of adequate fuel reserves in the tanks. Beryllium, boron and their hydrogen compounds are not readily available and are little

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TABLE 53

Heating Values of Certa n Elements [1]

1 Элемент	2 Символ	3 Плотность	4 Теплотворная способность $Q_{\text{в}}$		7 Состояние окисла
			5 ккал/кг	6 ккал/л	
8 Водород	H	0,07	28000*	2110	Газообразное 17
9 Бериллий	Be	1,85	15000	27750	Твердое 18
10 Бор	B	2,30	13056	31400	»
11 Литий	Li	0,53	10300	5450	»
12 Алюминий	Al	2,7	7200	19700	»
13 Магний	Mg	1,43	6000	8550	»
14 Кремний	Si	16 2(аморфный)	7160	14350	»
15 Углерод	C	1,8—2,1	7840	15700	Газообразное 19

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*For hydrogen Q_n.

1) Element; 2) symbol; 3) density; 4) heating value Q_v; 5) kcal/kg; 6) kcal/liter; 7) state of oxide; 8) hydrogen; 9) beryllium; 10) boron; 11) lithium; 12) aluminum; 13) magnesium; 14) silicon; 15) carbon; 16) amorphous; 17) gaseous; 18) solid; 19) gaseous.

suited for large-scale use, so that the question of using them in fuels will apparently arise only in special cases.

In the light of the above, compounds of hydrogen with carbon — hydrocarbons, which have relatively high heating values and are available in virtually inexhaustible quantities, are used as fuels for air-breathing jet engines.

The heating values of hydrocarbon fuels depend on their elementary composition, which is associated first and foremost with their group composition.

The lower-limit heating value has been adopted as the basic thermochemical characteristic of hydrocarbon fuels. It is computed on the basis of the upper-limit heating value, which is determined calorimetrically, by correcting for the hydrogen content in the fuel in accordance with the formula

$$Q_\text{н} = Q_\text{в} - 50{,}45 \cdot \text{H},$$

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where H is the percentage content of hydrogen in the fuel.

In the case of individual hydrocarbons, the percentage hydrogen content in the fuel is found from the chemical formula; in the case of fuels, it is found by elementary analysis or may also be computed approximately from the density in accordance with the empirical formula

$$\% \ H. = 26 - 15 \rho_4^{20}.$$

The elementary composition of aviation jet fuels usually lies in the following range:

$$H = 12.4-15.3\%; \ C = 85-87.5\% \text{ and } S = 0.005-0.4\%.$$

The heating values of petroleum products may be determined very approximately on the basis of elementary composition by use of D.I. Mendeleyev's empirical formula

$$Q_{\text{н}} = 81 \ C\% + 246 \ H\% + 26 \ (S - O) \ \%,$$

where C, H, O and S are the percentage contents of the corresponding elements.

Approximate methods also exist for computing the heating values of fuels from their physical constants.

Thus, the heating value may be associated by empirical formulas with the density, as given by the Kragoe formula:

$$Q_{\text{н}} = 11 \ 088 + 757\rho - 2100\rho^2.$$

Using this formula, we obtain a 3 to 5% discrepancy between experimental and calculated values.

Reports have recently been published in which an attempt is made to express the lower-limit heating value as a function of density and aniline point [2].

Recently, V.I. Lavrent'yev [3] proposed a formula in which the heating value is found from the refractive index:

$$Q_{\text{н}} = 18 \ 600 - 5730 n_D^{20} \ \text{kcal/kg}.$$

The formula gives values on the high side for the heating values

of aromatic hydrocarbons (2-4% high), but produces excellent results for T-1, T-2 and T-4 jet fuels (discrepancies in the range from 0.2 to 0.5%).

In another formula proposed by V. I. Lavrent'yev, the refractive index and aniline point are taken into account:

$$Q_{\scriptscriptstyle \text{H}} = 7.5 T_{\text{A}} - 2865 n_D^{20} + 14\,080 \text{ kcal/kg}.$$

where T_A is the aniline point (^{o}C).

This formula gives a 0.3-1% error in determinations of the heating values of T-1 and T-2 fuels, but it gives good results for high-aromatic fuels and aromatic hydrocarbons. For paraffinic hydrocarbons and fuels, however, the error may reach 2%. Both formulas have been tested on 100 samples of fuel of the T-1 and T-2 types and on 20 individual hydrocarbons, and may be used to estimate heating value.

2. Heating Values of Hydrocarbons

The heating value of a jet fuel is composed of the heating values of the individual hydrocarbons of the various series forming the fuel. In this connection, let us examine the heating values of hydrocarbons having the same number of carbon atoms but belonging to different hydrocarbon series (Table 54).

As will be seen from Table 54, the lower-limit heating values of hydrocarbons with equal numbers of carbon atoms may differ by more than 1000 kcal/kg in the transition from hexane to benzene.

Table 55 lists the heating values of homologous series of hydrocarbons that may, on the basis of their boiling points, be found in broad-fraction turbojet fuels.

Recently, the use of hydrocarbon radicals as a high-calorie [exotic] fuel has been suggested. According to calculation, the low-limit heating value of the methyl radical is about 14,000 kcal/kg, that of ethyl is 12,000 kcal/kg, and that of propyl is 11,400 kcal/kg [4].

TABLE 54

Elementary Compositions and Heating Values of Hydrocarbons of Various Series [4]

1 Углеводород	2 Формула	3 Состав, %		4 Теплотворная способность°, ккал/кг	
		H	C	$Q_в$	$Q_н$
5 Гексан	C_6H_{14}	16,26	83,74	11560	10608
6 Гексен	C_6H_{12}	14,28	85,72	11450	10615
7 Циклогексан	C_6H_{12}	14,28	85,72	11150	10379
8 Бензол	C_6H_6	7,56	92,44	10000	9503

*Heating value from data on heat of combustion (kcal/gram-molecule).

1) Hydrocarbon; 2) formula; 3) composition, %; 4) heating value,* kcal/kg; 5) hexane; 6) hexene; 7) cyclohexane; 8) benzene.

TABLE 55

Heating Values in Homologous Series of Hydrocarbons [1, 4]

1 Ряд углеводородов	2 Теплотворная способность $Q_н$, ккал/кг			
	C_6	C_{10}	C_{12}	C_{16}
3 Парафины нормальные	10698	10570	10540	10503
4 Изопарафины	—	10535	10513	10484
5 Олефины нормальные	10615	10483	10470	10444
6 Нафтены моноциклические	10379	10375	—	10360
7 Нафтены бициклические	—	10200	—	—
8 Бензол и его гомологи	9593	9945	9917	—
9 Гомологи нафталина	—	9270	9475	—
10 Нафтено-ароматические углеводороды	—	9426	—	—

Note. The C_{10}, C_{12} and C_{16} isoparaffins are represented by the tetramethylalkanes, and the aromatic and naphthenoaromatic hydrocarbons with C_{10} and C_{12} are represented by n-butylbenzene, tetralin and ethylnaphthalene.

1) Hydrocarbon series; 2) heating value Q_n, kcal/kg; 3) normal paraffins; 4) isoparaffins; 5) normal olefins; 6) monocyclic naphthenes; 7) bicyclic naphthenes; 8) benzene and its homologs; 9) naphthalene homologs; 10) naphthene-aromatic hydrocarbons.

Methods of storing radicals at low temperatures are being developed.

The heating value of a fuel is associated with the ratio between its carbon and hydrogen contents — the quantity C/H. This relationship is shown in Fig. 56 on the basis of experimental data for individual hydrocarbons and aviation-turbine fuels. In motor and jet fuels, the ratio C/H varies in the range from 5.7 to 6.7, while the lower-limit heating value varies accordingly from 10,000 to 10,500 kcal/kg.

In paraffins, the lower-limit heating value differs from the upper limit by an average of 770-800 kcal/kg; in olefins and naphthenes, the range is 750-770 kcal/kg, and for benzene it is 380 kcal/kg.

In paraffinic hydrocarbons, the heating value diminishes with increasing boiling point, as does the hydrogen content in accordance with the composition formula C_nH_{2n+2}. In monocyclic naphthenes, this variation is considerably smaller. In the benzene homologous series, the heating value increases as we pass toward higher homologs due to the side chain. Thus, it is 9593 kcal/kg for benzene and 9945 kcal/kg for n-butylbenzene. Bicyclic aromatic hydrocarbons have a low heating value of the order of 9500 kcal/kg.

For example, the heating value of butylnaphthalene is 9535 kcal/kg, while that of isoamylnaphthalene is 9601 kcal/kg.

The heating value referred to a unit volume — the so-called per-liter heating value — varies as a function of chemical composition to an even greater degree than does the unit-weight heating value. It is the product of the unit-weight heating value by the density: $Q_n \cdot \rho$.

Thus, on transition from the paraffinic to the naphthenic and aromatic hydrocarbons, the unit-volume heating value increases more sharply than the unit-weight heating value diminishes.

Table 56 shows the changes in unit-weight and unit-volume heating value in various hydrocarbon series.
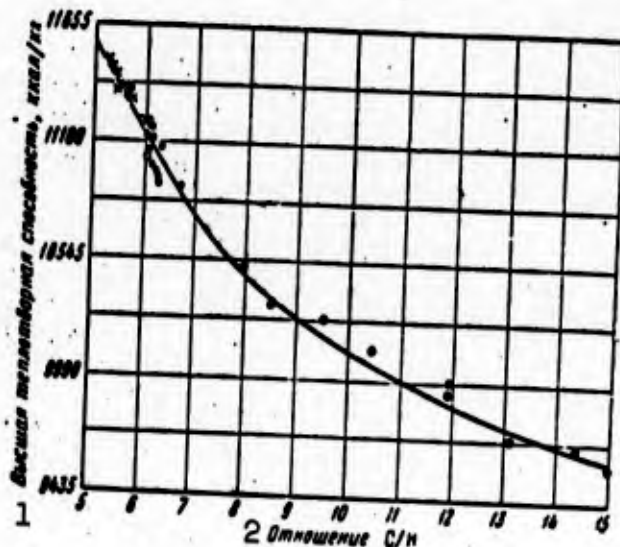
Fig. 56. Upper-limit heating values
of hydrocarbons in various series as
functions of C/H ratio. x) Paraffins;
0) naphthenes; ◑) aromatic hydrocar-
bons; ●) petroleum products. 1) Up-
per-limit heating value, kcal/kg; 2)
C/H ratio.

In bicyclic naphthenes, such as decalin, the heating value re-
ferred to unit volume is 1010-1360 kcal higher than that of decane.
This is particularly characteristic for cis-decalin, which has a high
density (0.89) and a heating value of 10,225 kcal/kg. Benzene homologs
such as butylbenzene are inferior to the bicyclic naphthenes. Mono-
cyclic naphthenes have no particular advantage as regards their unit-
volume heating values.

The naphthenoaromatic hydrocarbons, e.g., tetralin, have high
unit-volume heating values in combination with much lower unit-weight
heating values. This applies to an even greater degree to the naphtha-
lene homologs such as methylnaphthalene.

The unit-volume heating value changes not only as we pass from
one homologous series of compounds to another, but also within the
limits of a single group of compounds having the same number of carbon
atoms, e.g., among different isomers. Here, there is virtually no de-
crease in the unit-weight heating value (Table 57). Thus, the unit-

weight heating values of decane and 3,3,4,4-tetramethylhexane range
from 10,570 to 10,535 kcal/kg, while the latter's unit-volume value is
535 kcal higher than that of the former. A similar pattern is observed
in the olefins and naphthenes.

TABLE 56

Changes in Unit-Weight and Unit-Volume Heating
Values [4]

1 Углеводород	2 Формула	3 Плотность ρ_4^{20}	4 Теплотворная способность	
			5 ккал/кг	6 ккал/л
7 н. Декан	C₁₀H₂₂	0,7299	10 570	7680
8 Децен-2	C₁₀H₂₀	0,7421	10 483	7740
9 Бутилциклогексан	C₁₀H₂₀	0,7992	10 375	8260
10 Декалин (транс)	C₁₀H₁₈	0,872	10 165	8750
11 Декалин (цис)	C₁₀H₁₈	0,800	10 225	9100
12 Бутилбензол	C₁₀H₁₄	0,8603	9 945	8550
13 Тетралин	C₁₀H₁₂	0,9731	9 723	9450
14 Метилнафталин	C₁₁H₁₀	1,025	9 394	9625
16 Керосин авиационный	—	15 (при 14°) 0,81	10 250	8300

1) Hydrocarbon; 2) formula; 3) density ρ_4^{20}; 4)
heating value; 5) kcal/kg; 6) kcal/liter; 7) n-
decane; 8) decene-2; 9) butylcyclohexane; 10)
decalin (trans); 11) decalin (cis); 12) butylben-
zene; 13) tetralin; 14) methylnaphthalene; 15) at
14°; 16) aviation kerosene.

In a number of cases, the specific gravity of the hydrocarbons
increases with increasing complexity of the branches and the appear-
ance of quaternary atoms (n-decane 0.72 and 3,3,4,4-tetramethylhexane
0.78), but this phenomenon is not always observed. Thus, for example,
2,2,5,5-tetramethylhexane has a density of 0.718.

The unit-volume heating values of the alkanes, alkenes, and naph-
thenes depend on the structure of the carbon-atom skeleton.

3. Heating Values of Jet Fuels

The heating values of jet fuels vary over a narrower range than
those of the hydrocarbons and hydrocarbon groups composing the fuel.
This will be seen at once from the data of Tables 55 to 58.

TABLE 57

Variation of Unit-Volume Heating Value in Isomeric C_{10} Hydrocarbons [4]

1 Углеводород	2 Плотность ρ_4^{20}	3 Объемная теплотворная способность, ккал/л
4 Парафины		
5 н. Декан	0,7299	7680
6 2,2,2-Триметилэтилпентан	0,7818	8210
7 3,3,4,4-Тетраметилгексан	0,7824	8215
8 4-Метилнонан	0,7323	7690
9 2,2,3,3,4-Пентаметилпентан	0,7801	8200
10 2,7-Диметилоктан	0,7242	7600
11 2,2,3,4,4-Пентаметилпентан	0,7670	8060
12 2,2,5,5-Тетраметилгексан	0,71800	7540
13 Олефины		
14 Децен-2	0,7421	7750
15 3,4,4,5-Тетраметилгексен-2	0,7800	8110
16 2,2,3,4-Тетраметилгексен-3	0,7706	8000
17 3,4,5,5-Тетраметилгексен-2	0,7679	7990
18 3,7-Диметилоктен-1	0,7306	7700
19 Нафтены		
20 н. Бутилциклогексан	0,7092	8260
21 1,2,3,4-Тетраметилциклогексан	0,82219	8500
22 втор. Бутилциклогексан	0,8131	8430

1) Hydrocarbon; 2) density ρ_4^{20}; 3) unit-volume heating value, kcal/liter; 4) paraffins; 5) n-decane; 6) 2,2,2-trimethylethylpentane; 7) 3,3,4,4-tetramethylhexane; 8) 4-methylnonane; 9) 2,2,3,3,4-pentamethylpentane; 10) 2,7-dimethyloctane; 11) 2,2,3,4,4-pentamethylpentane; 12) 2,2,5,5-tetramethylhexane; 13) olefins; 14) decene-2; 15) 3,4,4,5-tetramethyl-hexene-2; 16) 2,2,3,4-tetramethyl-hexene-3; 17) 3,4,5,5-tetramethyl-hexene-2; 18) 3,7-dimethyloctene-1; 19) naphthenes; 20) n-butylcyclohexane; 21) 1,2,3,4-tetramethylcyclohexane; 22) sec-butylcyclohexane.

The difference between the volumetric heating values of paraffinic and aromatic hydrocarbons is about 10%.

According to the direct bomb-calorimeter determinations of Ya.B. Chertkov, V.N. Zrelov and V.V. Rudakov [6], the lower-limit heating values of the fuel fractions of Soviet petroleums take the values given

Heating Values of a Number of Fuels and the Hydro-
carbon Groups Composing Them [5]

1 Топливо или группа углеводородов	2 Плотность при 15,5°	3 Пределы кипения	4 Групповой состав, %			8 Теплотворная способность	
			5 ароматические	6 нафтены	7 парафины	9 ккал/кг	10 ккал/л
11 Авиационное топливо	0,7650	60—270	—	—	—	10350	7900
12 Авиационный керосин	0,7940	155—270	19,4	39,2	41,4	10260	8135
13 Концентрат парафиновых углеводородов	0,7475	150—265	2,6	5,2	92,2	10360	7723
14 Концентрат нефтено-парафиновых углеводородов	0,7910	160—270	1,4	51,9	46,7	10300	8133
15 Концентрат ароматических углеводородов	0,8645	166—253	75,2	11,4	13,4	9860	8320
16 Авиационный бензин	0,7200	60—180	—	—	—	10520	7582
17 Дизельное топливо	0,8700	200—325	—	—	—	10050	8720

1) Fuel or hydrocarbon group; 2) density at 15.5°;
3) boiling range, °C; 4) group composition, %; 5)
aromatic; 6) naphthenes; 7) paraffins; 8) heating
value; 9) kcal/kg; 10) kcal/liter; 11) aviation
fuel; 12) aviation kerosene; 13) paraffin-hydrocar-
bon concentrate; 14) naphthenoparaffinic-hydrocar-
bon concentrate; 15) aromatic-hydrocarbon concen-
trate; 16) aviation gasoline; 17) diesel fuel.

in Tables 59 and 60 as functions of their chemical and fractional com-
position.

The variation of the unit-volume heats of combustion for the same
petroleums is given in Table 61.

Depending on group and fractional composition, the difference in
the unit-volume heat of combustion may run as high as the order of
1000 kcal/liter.

The unit-weight heat of combustion of aromatic hydrocarbons dimin-
ishes with increasing number of rings in the molecule. Thus, addition
of one aromatic ring results in the heat of combustion dropping by an
average of 210-260 kcal/kg for hydrocarbons with one or two carbon
atoms in the side chains.

Thus, the dependence of the unit-volume and unit-weight heating
values of the fuels on their group and fractional compositions is

TABLE 59

Lower-Limit Heating Values (kcal/liter) for Hydrocarbon Fractions [6]

1) Исходные продукты	2) Парафиновые				3) Нафтеновые (Пределы кипения фракции, °C)				5) Моноциклические ароматические			
	100—150	150—200	200—250	250—300	100—150	150—200	200—250	250—300	100—150	150—200	200—250	250—300
6 Бакинские нефти	7850 / 7930	8170	8560	—	7820 / 8130 / 8490	8170 / 8250 / 8320 / 8480 / 8550	8370 / 8240 / 8550 / 8520 / 8540	8670 / 8570 / 8850 / 8620 / 8620	8210	8690 / 8470 / 8950	8950 / 8940 / 8990 / 8590	9160 / 9050 / 9360 / —
7 Грозненские нефти	7730	8170	8320	—	7420	7700	8120	8470	8480	8650	8610	9090
8 Приволжские нефти	7950	7630	8070	8240	7490	8620	7630 / 8040	7870	8290	8310	8680	8650
9 Дальневосточные нефти	—	—	—	—	—	8290	8480	—	—	8700	8901	—
10 Продукты переработки каменного угля	—	—	—	—	—	8280	8680	8680	—	8670	9090	9260
11 Продукты каталитического крекинга и алкилирования	— / 7910	8140 / 7960	8330 / 8130	— / 8270	—	8050	8640 / 8230 / 8450	—	—	8480 / 8810	8710 / 8860	9010

1) Initial products; 2) paraffinic; 3) naphthenic; 4) boiling range of fraction, °C; 5) monocyclic aromatic; 6) Baku petroleums; 7) Grozny petroleums; 8) Volga petroleums; 9) Far Eastern petroleums; 10) coal-distillation products; 11) products of catalytic cracking and alkylation.

TABLE 60

Lower-Limit Heating Values (kcal/kg) for Hydrocarbon Fractions [6]

1 Исходные продукты	2 Парафиновые				3 Нафтеновые				5 Моноциклические ароматические			
4 Пределы кипения фракции, °C	100—150	150—200	200—250	250—300	100—150	150—200	200—250	250—300	100—150	150—200	200—250	250—300
6 Бакинские нефти	10 760 / 10 770 / 10 620	10 720 / 10 700	10 680	—	10 250 / 10 290 / 10 350	10 300 / 10 420 / 10 380 / 10 400 / 10 320 / 10 390	10 320 / 10 270 / 10 340 / 10 330 / 10 450 / 10 300 / 10 320	10 300 / 10 340 / 10 330 / 10 320 / 10 334 / 10 260	9 880	9 900 / 9 950 / 9 960 / 9 670	9 850 / 9 880 / 9 950 / 9 843	9 885 / 9 960 / 9 990 / 9 790
7 Грозненские нефти	10 610	10 630	10 600	—	10 000	10 110	10 190	10 300	9 960	9 880	9 950	9 930
8 Приволжские нефти	10 770	10 710	10 590 / 10 665	10 470	10 210	10 200	10 130 / 10 230	10 120	9 830	9 950	9 910 / 9 850	9 880
9 Дальневосточные нефти	—	—	—	—	—	10 370	10 370	—	—	9 860	9 880	—
10 Продукты переработки каменного угля	—	—	—	—	—	10 370	10 310	10 130	—	9 890	9 910	9 890
11 Продукты каталитического крекинга и алкилирования	10 490	10 700 / 10 620 / 10 510	10 480	10 300	—	10 320 / 10 370	10 460 / 10 400	10 320	—	9 670 / 10 020	9 840 / 9 900	9 790

1) Initial products; 2) paraffinic; 3) naphthenic; 4) boiling range of fraction, °C; 5) monocyclic aromatic; 6) Baku petroleums; 7) Grozny petroleums; 8) Volga petroleums; 9) Far Eastern petroleums; 10) coal-distillation products; 11) products of catalytic cracking and alkylation.

clearly indicated by the data given above.

The heating values of jet fuels lie in the range from about 10,250 to 10,350 kcal/kg. When paraffinic and olefinic hydrocarbons are used, the heating value may be raised to 10,400-10,500 kcal/kg. Thus, a paraffin-olefin fuel with a heating value of 10,400 to 10,500 in combination with a specific gravity of 0.77 to 0.80 may be produced starting with mixtures of normal and isomeric petroleum paraffins and from products of synthesis from CO and H_2.

TABLE 61

Ranges of Variation of Lower-Limit Heating Value
for Fifty-Degree Fractions [6]

1 Пределы кипения фракции, °C	2 Парафиновые		3 Нафтеновые		4 Моноциклические ароматические	
	5 ккал/кг	6 ккал/л	5 ккал/кг	6 ккал/л	5 ктал/кг	6 ккал/л
100—150	10 770—10 400	7950—7730	10 350—10 000	8490—7420	9960—9830	8480—8210
150—200	10 720—10 510	8170—7630	10 420—10 110	8620—7700	10020—9670	8950—8310
200—250	10 680—10 480	8560—8070	10 460—10 130	8680—7630	9950—9840	9000—8610
250—300	10 470—10 300	8270—8240	10 340—10 120	8850—7870	9090—9790	9360—8650

1) Boiling range of fraction, °C; 2) paraffinic;
3) naphthenic; 4) monocyclic aromatic; 5) kcal/kg;
6) kcal/liter.

The transition to fuel heating values above 10,500 to 10,600 kcal/kg with a density no lower than 0.77 presents considerable difficulty.

For example, propane, a representative of the light hydrocarbons, has a density of 0.50 together with a heating value of 11,040 kcal/kg and a low boiling point (—42°), which excludes the use of a propane-based fuel in contemporary engines.

The maximum flying time depends on the specific fuel consumption. In turn, however, the specific fuel consumption is determined by the type of the engines used and their economy. This is illustrated by the following data:
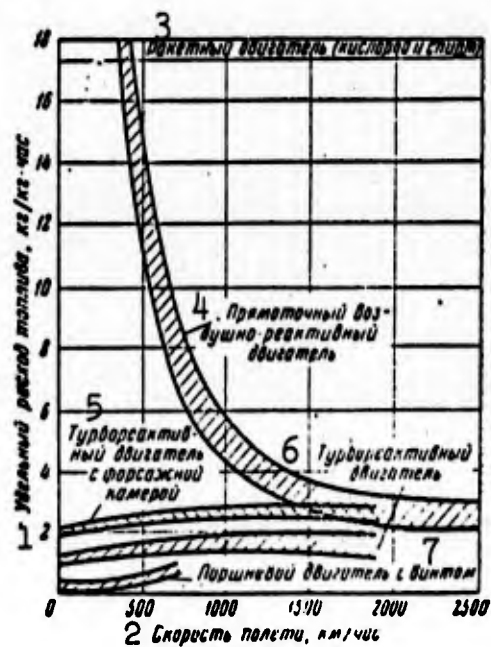
Fig. 57. Specific fuel con-
sumption for various aviation
power plants as a function of
flight speeds. 1) Specific
fuel consumption, kg/kg·hr; 2)
flight speed, km/hr; 3) rocket
engine (oxygen and alcohol);
4) ramjet engine; 5) augmented
turbojet engine; 6) turbojet
engine; 7) piston engine with
propeller.

Aviation engine	Specific fuel consumption, kg/hour·kg
Piston............................	0.7-0.9
Turbojet...........................	0.9-1.5
Intermittent [ramjet].............	4.1

Specific fuel consumption is shown in Fig. 57 as a function of
flight speed for various power-plant types. The data of this figure
would be properly regarded not as absolute, but as comparative quan-
tities.

All other factors the same, the specific fuel consumption depends
on the heating value Q_n of the fuel in accordance with the formula

$$c_{ud} = \frac{3600 \cdot g_\tau}{\frac{1}{g}\left\{ \sqrt{2g\,427\,\eta_g\eta_l\frac{Q_n}{\alpha L_0} + v^2} - v\right\}}.$$

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The higher the heating value of a fuel, the lower will be its specific consumption and the greater the flight range. Flight range is also determined by the density of the fuel, on which the amount carried on board the aircraft depends. Consequently, to achieve the maximum flight range with a given aircraft system, we must select the optimum density and heating value for the fuel.

In recent years, paraffinic hydrocarbons have been proposed for use as jet fuel, since they produce, on combustion, a colorless flame that possesses a lower radiation intensity; this makes it possible to burn the fuel at higher temperatures and in combustion chambers having smaller volume and weight [7, 8, 9].

An obstacle to the use of normal paraffins, which can be extracted easily from petroleum, is their high freezing temperatures. However, normal paraffins from C_{10} to C_{20} can be converted into isoparaffins.

Thus, it was shown in the studies of Ya.M. Paushkin and Kh.Ya. Orlov that normal paraffins with the composition C_{15}-C_{18} and freezing temperatures of $+18^{\circ}$ can be converted into isoparaffins of the same composition having an initial freezing point of -43°, a specific gravity of 0.80, and a lower-limit heating value of 10,500 kcal/kg. Isomerization is conducted at 380° and 20 atmospheres under hydrogen pressure over tungsten sulfide [10].

<div align="center">REFERENCES</div>

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Manu-
script
Page   [List of Transliterated Symbols]
No.

175   н = n = nizhniy = lower-limit

175   в = v = vysshiy = upper-limit

187   уд = ud = udel'nyy = specific

Chapter 5

INORGANIC AND ELEMENTARY-ORGANIC SUBSTANCES
HAVING HIGH HEATING VALUES WHICH
CAN BE EMPLOYED AS FUELS

1. General Information

There are only very few elements and their compounds which have a heating value in excess of 10,000-10,500 kcal/kg, which corresponds to a hydrocarbon fuel (combustible). Among these elements we find hydrogen, boron, beryllium, some of their compounds, and certain elementary-organic compounds of boron and beryllium.

Figure 58 shows the heating value and combustion temperature of a series of elements in oxygen in order of diminishing molecular weight.

However, the practical possibility, the area, and the means of using high heating-value elements and their compounds as reaction fuels have not yet been adequately studied.

Nevertheless, it should be pointed out that as early as 1946 it was reported that in the USA development had been begun on boron-based fuels for military aircraft [1]. The possible components of such fuels were listed as pentaborane B_5H_9 and aluminum borohydride $Al(BH_4)_3$.

Later on there were repeated reports dealing with the general nature of the work being done along these lines. In 1955 there were press reports also to the effect that the aluminum borohydride was being recommended for use as an ignition and combustion initiator for aviation fuels [2].

In 1956, reports appeared [3] that chemical plants in the USA were

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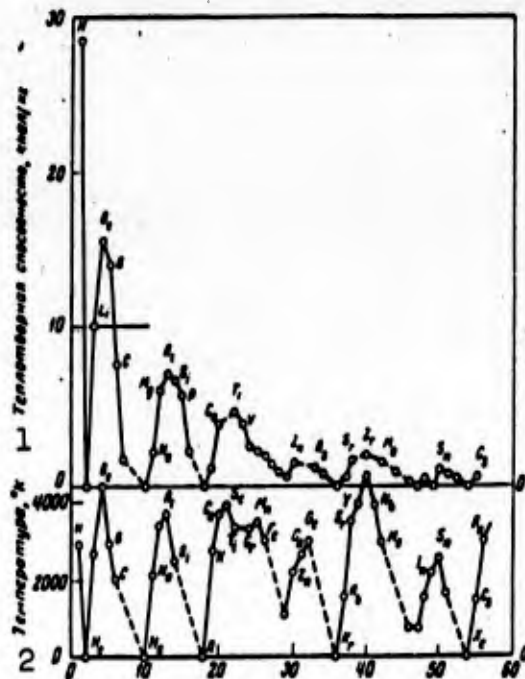
Fig. 58. Heating value and combustion
temperature of the elements in oxygen as
a function of atomic number. 1) Heating
value, kcal/kg; 2) temperature, ^{O}K.

producing, or preparing for production, new types of chemical fuels
for aviation engines and guided missiles. It was stated that in con-
nection with the utilization of new types of fuels (combustibles) it
would be possible sharply to increase engine power (by at least 50%)
and thus to increase flight range.

Among these fuels (combustibles) compounds of boron with hydrogen
and lithium are dominant.

It is stated that the best among these synthetic fuels (combus-
tibles) for direct-flow [ramjets] engines of the future will be a com-
pound of boron with hydrogen — pentaborane — whose heating value is
54% higher than that of gasoline, and the flight range with this com-
bustible may be increased by 40% in comparison with a fuel (propellant)
like kerosene [3].

It is assumed that the cost of the pentaborane, once production
is in full swing, will cost on the order of $2000 per ton [3]. Another

advantage of pentaborane is its comparatively high rate of combustion in comparison with gasoline, thus making it possible to utilize shorter combustion chambers and, consequently, lighter engines.

Note is also taken of the fact that suspensions of magnesium and aluminum and their alloys in hydrocarbon fuels may be of interest. There is confirmation of the fact that tests were carried out on such suspensions, containing approximately 50% metal in octane, and that the potential engine thrust in this case can be increased by more than 50% in comparison with hydrocarbon fuels [3].

Liquid compounds of boron with hydrogen may be regarded directly as fuels or as fuel components in a solution of hydrocarbon, and this applies equally to solid compounds of boron with hydrogen and beryllium or powders of boron and beryllium in the form of suspensions in petroleum products, since such systems have high heating values. However, the practical possibilities of using such fuels is associated with a number of operational characteristics as well as problems of raw-material and manufacturing facilities.

In this connection, it would be expedient to consider the physico-chemical properties and basic methods of producing high heating-value boron, beryllium, and their compounds.

2. Boron and Beryllium

a) Boron

The heating value of boron is 13,956 kcal/kg (assuming a heat of formation of its oxide in the solid state at 302 kcal/g-mole). Boron belongs to the comparatively common elements. Its occurrence in the Earth's crust is estimated as ranging between $1.5 \cdot 10^{-4}$-$3 \cdot 10^{-4}$%. In nature it is found in the form of oxygen compounds — borax $Na_2B_4O_7 \cdot 10H_2O$ and certain others [4]. The worldwide output of boron compounds is measured in hundreds of thousands of tons annually. The USA in 1956

produced 857 thousand tons of boron-bearing raw materials. In 1955, 839 thousand tons of borates ($Na_2B_4O_7 \cdot 4H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $Ca_2B_6O_{11} \cdot 5H_2O$ and others) were produced, and these contained 252 thousand tons of boric acid anhydride B_2O_3. In 1960, more than 1 million tons of borates were produced.

Boron is known both as a crystalline solid and an amorphous powder. The best method for the derivation of the amorphous boron is based on the reduction of B_2O_3 with metallic magnesium [5]:

$$B_2O_3 + 3Mg \rightarrow 3MgO + 2B.$$
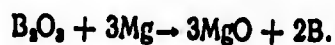
By using the threefold excess of boric-acid anhydride and with the subsequent extensive treatment of the products of the reaction with HCl, HF, and H_2SO_4, it is possible to obtain 94-95% pure boron. By additional purification of the boron through fusion with the excess B_2O_3 it was possible to obtain 98% and even 99% boron containing only traces of the magnesium [4, 5].

In the reduction of the boric acid anhydride with other metals such as, for example, calcium or aluminum, the product is always fouled to some extent by such impurities as the borides of these metals. In particular, insoluble aluminum borides, formerly numbered among the crystalline forms of boron, are formed primarily in the aluminum-heat reduction. Apparently, the magnesium-heat method is the most convenient from the standpoint of boron derivation [5].

Of the remaining methods of boron derivation we can also mention the reduction of B_2O_3 with lithium hydride, as well as the reduction of KBF_4 with metallic sodium [6, 7].

The boron obtained by the magnesium-heat method can be purified by roasting it in a vacuum at 1800-2000°. In this case, the magnesium borides such as, for example, MgB_{12}, decompose and the result is a product that contains no less than 99.5-99.8% B.

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The electrochemical method of obtaining boron [8], developed in 1929, involves the cathode separation of boron during the electrolysis of a mixture of borate alloys containing MgO with an admixture of MgF_2. This method yields a product containing 89-92% boron.

There are indications that a purer form of boron (up to 99.5%) can be obtained by the electrolysis of potassium fluoroborate in a mixture with KCl at 800-850° with a copper or molybdenum cathode [9].

Of the methods capable of producing the purest forms of boron, we should mention first of all the reduction of boron halides with hydrogen on the basis of the following reaction

$$2BX_3 + 3H_2 \rightarrow 2B + 6HX.$$

For example, in the reduction of BBr_3 with hydrogen in a quartz tube at 800° we obtain a product containing 98.9% boron which yields approximately 80% [10].

During the first stage, apparently, diborane B_2H_6 is obtained, and this is subsequently subjected to cracking which results in the formation of boron.

The thermal dissociation of BBr_3 at 800-1600° was used to obtain high-purity crystalline boron [11].

The physicochemical properties of elementary boron are determined to a great extent by the purity of the product, which in turn is associated with the method employed to obtain the product. Many properties of boron have not yet been adequately studied.

The purest specimens, whether of amorphous or crystalline boron, are black in color. On the other hand, the ordinary so-called "amorphous" boron is brown in color, and this is probably associated with the presence of oxides.

Elementary boron (amorphous and crystalline) is produced on an industrial scale in the USA. Amorphous boron contains 95-97% of the basic

substance, and the crystalline form contains no less than 99% boron.

The amorphous boron obtained by the magnesium-heat method does not burn easily and in a number of cases is of inadequate purity; it is for this reason that such great interest has been expressed in the derivation of boron by the cracking of diborane and other boranes at a temperature of 700°. In this case, the reaction apparently takes place with the formation of pure boron as well as with the formation of a certain quantity of solid boron hydrides (boranes):

$$B_2H_6 \nearrow^{2B + 3H_2}_{\searrow (BH_x)_y + H_2}$$
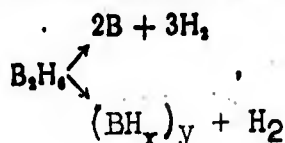
where $\underline{x}$ is less than unity.

During the reaction, the boron is deposited on the walls of the reactor in the form of particles having dimensions of 0.025-0.5 μ [11].

The chemical properties of the boron are strong functions of the degree of its crystallinity and of its purity. "Amorphous" boron oxidizes slowly on heating in air and ignites if heated above 800°. Large boron crystals are heat resistant even in the case of substantially higher temperatures. Hydrochloric and hydrofluoric acids do not attack boron even in the case of prolonged boiling. Hot concentrated nitric acid oxidizes crystalline boron slowly, but it oxidizes amorphous boron quickly.

Chlorine, fluorine, and fluorine compounds with chlorine easily oxidize boron, with the formation of halides (bromine at 700°, chlorine at 410°, fluorine at room temperature). At a temperature in excess of 1000° boron yields a nitride with nitrogen. Boron reacts with carbon only at temperatures in excess of 1800-2000°.

Boron reacts at high temperatures with the majority of metals and their oxides, forming various borides.

At 25°, boron has a density ranging between 2.30 and 2.34 (various preparations). The melting point of boron is $2075 \pm 50^{\circ}$, the boiling point is 2500°, and the coefficient of thermal expansion for boron between 20 and 750° is $8.3 \cdot 10^{-6}$; the entropy of boron is 1.403 (for crystalline) and 1.564 (for amorphous) cal/mole·deg at 25°; the heat capacity is 2.650 (for crystalline) and 2.858 (for amorphous) cal/mole·deg.

b) Beryllium

Beryllium is a white and extremely hard metal having a specific weight of 1.85, a melting point of 1285°, and a boiling point of 2970°. The melting point of beryllium oxide is 2570°, and the boiling point is 3900°. At the moment beryllium is used to some extent in alloys of metals to harden the latter, and for certain other purposes as well [12].

The occurrence of beryllium in the Earth's crust is estimated at $4 \cdot 10^{-4}\%$, by weight, i.e., approximately the same as cadmium $(5 \cdot 10^{-4}\%)$, and more by a factor of four than iodine $(1 \cdot 10^{-4}\%)$, and less by a factor of five or six than lead $(1.6 \cdot 10^{-3}\%)$. Metallic beryllium burns in oxygen, liberating a great quantity of heat:

$$Be + \frac{1}{2}O_2 \rightarrow BeO + 143\,kcal.$$

The heat of formation of solid beryllium oxide, according to certain data, is +145 kcal/mole [12], and according to other data it is equal to $+143 \pm 1$ kcal/mole, the latter figure being regarded as more reliable. The melting point of beryllium oxide is $2550 \pm 25^{\circ}$, and the boiling point is $4260 \pm 160^{\circ}$. The heat of fusion of beryllium oxide is $+17 \pm 1.4$ kcal/mole, and the heat of vaporization is ±156.6 kcal/mole.

The two following equations have been proposed for the specific heat of beryllium oxide:

$$C_p = 8{,}45 + 4{,}1 \cdot 10^{-3} \cdot T - 3{,}17 \cdot 10^{-5} \cdot T - 2$$
$$C_p = 9{,}471 + 2{,}090 \cdot 10^{-3} \cdot T.$$

For liquid beryllium oxide the specific heat, at 2600°, is 16 cal/mole·deg.

When fluorine and beryllium are used as oxidizers in rocket propellants, beryllium fluoride is formed according to the following equation:

$$Be + F_2 \rightarrow BeF_2.$$
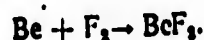
The heat of formation for solid beryllium fluoride is 240 kcal/mole; according to other data, it is 241.8 kcal/mole. The heat of sublimation for beryllium fluoride is 56.64 kcal/mole, the melting point is 787°, and the boiling point is 1327°.

In nature, beryllium is found in the form of the beryl mineral $3BeOAl_2O_3 \cdot 6SiO_2$. The worldwide output of beryllium (excluding the USSR) was [12]:

$$
\begin{array}{rl}
1936.................. & 480 \text{ tons} \\
1950.................. & 7300 \text{ tons} \\
1956.................. & 14000 \text{ tons}
\end{array}
$$

Of the 14,000 tons produced in 1956, almost 13,000 tons came from the USA.

The rapid growth in the exploitation of beryllium ores is associated with the utilization of beryllium in atomic engineering and in aircraft and rocket building. Studies are also underway to determine the possibility of using beryllium as a constituent for solid rocket propellants.

Industrially, metallic beryllium is produced by the reduction of beryllium fluoride with magnesium according to the following reaction:

$$BeF_2 + Mg \rightarrow Be + MgF_2 + 22 \text{ kcal}.$$
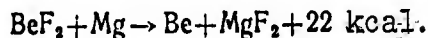
This is the basic method used in the USA ar Great Britain. The reduction is carried out in graphite retorts (at a temperature ranging between 900 and 1300°). Beryllium comes in the form of ingots and is

freed of its impurities by vacuum fusion, after which it contains no less than 99.5% Be, and the purity of the metal attains 99.8% after vacuum distillation. Metallic beryllium is obtained industrially also by the electrolysis of fused salts $NaCl-BeCl_2$ or BeF_2-NaF, but this method is not used as frequently. Beryllium is fashioned into ingots, foil, and powder with the average particle dimensions between 14 and 15 μ [12].* As dust, beryllium or its oxide and its salts are extremely toxic. These can produce dermatitis and acute irritation of the lungs.

Beryllium forms a compound with hydrogen — beryllium hydride BeH_2 [13] — a white-colored solid that is insoluble in ether, toluene, and isopentane. Beryllium hydride is quite stable in the air of the atmosphere below temperatures of 80-100°, but it reacts vigorously with water.

We know of such metal-organic beryllium compounds as methyl-beryllium hydride $HBeCH_3$ and dimethylberyllium $Be(CH_3)_2$, as well as beryllium borohydride $Be(BH_4)_2$. Beryllium borohydrides are also being considered as high heating-value additives for fuels.

3. Compounds of Boron with Hydrogen

Compounds of boron with hydrogen are substances which are of interest from the standpoint of their high heating values (in excess of 15,000 kcal/kg). Boranes occur as gaseous, liquid, and solid compounds. Some are unstable in air, whereas others are comparatively stable; however, in comparison with hydrocarbons, boranes are chemically substantially more active.

The properties of borohydrides and other important compounds based on the borohydrides are presented in Table 62.

The thermochemical properties of boranes and borohydrides are not adequately covered in the literature. Frequently, published data also exhibit great divergence. A heat of formation of 6.73 $\pm$ 0.52 kcal/g·mole

is cited for diborane [14], for aluminum borohydride this value is 7.2
kcal/g·mole, and for lithium borohydride this value is 42.08 kcal/g·mole
[15]. Diborane is described as endothermic which is highly likely,
since the pyrolysis of diborane is accompanied by the liberation of
heat.

TABLE 62

Characteristics of Certain Stable Liquid and Solid
Compounds of Boron with Hydrogen [16-24]

1 Соединение	2 Форму	3 Т. пл., °C	4 Т. кип., °C	5 Уд. вес при 20°	6 Упругость пара, мм рт.ст.	7 Общая характеристика
8 Пентаборан стабильный	B_5H_9	—46,6	60. 15,1 (при 131 мм)	0,610 (0°) 0,63(16°)	66 (10°)	15 Не воспламеняется на воздухе при 0—10°; подой очень медленно разлагается
9 Декаборан	$B_{10}H_{14}$	+99,7	213 156° (при 162 мм)	0,92 (99°)	19 (100°)	16 Не воспламеняется, не разлагается; медленно гидролизуется водой
10 Боразол	$B_3N_3H_6$	—58	53	0,8519		17 Химически стоек; растворим в холодной воде без химического взаимодействия; при нагревании гидролизуется
11 Боргидрид алюминия	$Al(BH_4)_3$	—65,4	44,5	0,5588 (13,8°)	11,5 (0°)	18 Бурно реагирует с водой и кислородом воздуха
12 Боргидрид бериллия	$Be(BH_4)_2$	+31	91,3	—	—	То же 19
13 Боргидрид лития	$LiBH_4$	+273	—	0,666	—	20 Устойчив к кислороду в отсутствие влаги

1) Compound; 2) formula; 3) melting point, °C; 4)
boiling point, °C; 5) specific weight, at 20°C; 6)
vapor tension, mm Hg; 7) general characteristic;
8) pentaborane, stable; 9) decaborane; 10) bora-
zole; 11) aluminum borohydride; 12) beryllium boro-
hydride; 13) lithium borohydride; 14) at; 15) does
not ignite in air at 0-10°; decomposes very slowly
in water; 16) does not ignite, does not decompose;
hydrolyzes slowly in water; 17) chemically stable;
soluble in cold water without chemical reaction;
hydrolyzes in heated water; 18) reacts vigorously
with water and the oxygen in the air; 19) the same;
20) stable in oxygen, in the absence of moisture.

The boranes burn and liberate great quantities of heat, and their
heating value can be calculated in accordance with the combustion equa-
tion if we know the heat of formation of the boron oxide, i.e.:

TABLE 63

Heat of Formation of B_2O_3

1 Авторы	Теплота образования, 2 ккал/моль	Ссылка на 3 литературу
4 Бертло	279,9	[25]
5 Рот, Бергер	349	[26]
6 Рот	345	[27]
7 Тод, Мюллер	335	[28]
8 Прозен, Джонстон	303	[14,29]
9 Эгерглюс, Монрое	281,1	[30]
10 Джонстон, Хёрш, Керр	302	[31]

1) Authors; 2) heat of formation, kcal/mole; 3) literature reference; 4) Berthelot; 5) Roth, Berger; 6) Roth; 7) Todd, Muller; 8) Prosen, Johnston; 9) Eggerglus, Monroe; 10) Johnston, Hirsh, Kerr.

$$B_5H_9 + 6O_2 \rightarrow 2\frac{1}{2}B_2O_3 + 4\frac{1}{2}H_2O.$$
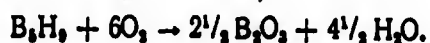
For the heat of formation of boric anhydride, various values are cited (Table 63).

Such divergence in data on the heat of formation of B_2O_3 can be explained by the experimental difficulties encountered in the determination of this heat of formation, the degree of purity of the boron preparations, and the completeness of their combustion. For the heat of vaporization of B_2O_3 we find values of 65.6 kcal/mole [32] and 77.6 kcal/mole [33].

Pentaborane B_5H_9 is referred to as "stable pentaborane," since among the boranes it is chemically comparatively stable. For example, prolonged storage of B_5H_9 at room temperature over a number of years has shown that stable pentaborane decomposes only slightly forming a small quantity of hydrogen and a solid residue. The slow decomposition of stable pentaborane becomes noticeable at 150°; rapid decomposition takes place at 300°. In air B_5H_9 is hypergolic, but this self-ignition does not always occur. However, a mixture of pentaborane vapors with pure oxygen ignites. The kinetics of this process were the subject of

a special work [34] in 1951.

The lower limit of explosion is a function of the pressure at which the gaseous mixture $B_5H_9-O_2$ is situated. The $B_5H_9-O_2$ mixture explodes at room temperature and this was observed at a total pressure of 3-6 mm Hg in the system; however, the occurrence of an explosion is a function of the composition of the fuel (combustible) mixture and the volume of the vessel [34] (Table 64).

Pentaborane hydrolyzes very slowly with water. Over a period of 72 hours, at 90°, incomplete hydrolysis takes place. Stable pentaborane is readily soluble in hydrocarbons, cyclohexane, and benzene.

Density ρ, surface tension σ, and viscosity η of the pentaborane can be calculated according to the following equations:

$$\rho = 674 - 0{,}00082\,T$$
$$\sigma = (71{,}1 - 0{,}1437\,T) \cdot \rho^{1/4}$$
$$\eta = 41{,}15 \cdot 10^{-5} \cdot \rho^{1/4} \cdot e^{1024\omega/T}$$

The following has been determined for pentaborane: heat of fusion, 1.466 kcal/mole; heat of vaporization, 7.7 kcal/mole; specific heat of liquid pentaborane, $C_p = 35.8$ cal/mole·deg; and specific heat of gaseous pentaborane, $C_p = 19$ cal/mole·deg; and in addition, the heat of formation for liquid pentaborane is +7.8 kcal/mole [4].

The heat of pentaborane combustion, determined in a bomb calorimeter, is 1078 kcal/mole or 17,100 kcal/kg for H_2O (liquid) and B_2O_3 (solid) [4].

Pentaborane combines with olefins, forming such alkyl derivatives as:

$$B_5H_9 + CH_2 = CH_2 \rightarrow B_5H_8C_2H_5$$
$$B_5H_9 + 2CH_2 = CH_2 \rightarrow B_5H_7(C_2H_5)_2$$
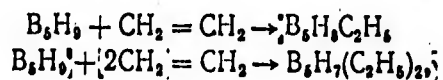
which have been recommended for utilization as fuels. Decaborane, as well as pentaborane, reacts with olefins and diolefins, forming the corresponding alkyl derivatives. Some of these derivatives are in the

liquid state and can be used as liquid propellants (fuels).

In addition to decaborane, we know of solid polymeric hydrides of boron ranging in composition from $(BH_{0.8})_x$ to $(BH_{1.5})_x$. These compounds are similar to the boranes in terms of a number of chemical properties.

Pentaborane B_5H_{11} is referred to as "unstable pentaborane," since it decomposes spontaneously at room temperature and forms B_2H_6, B_4H_{10}, B_5H_9, and $B_{10}H_{14}$, and ignites spontaneously in air. It is the least stable of the known boranes and its practical application is therefore difficult.

Decaborane $B_{10}H_{14}$. This completely stable solid material exhibits the greatest chemical stability in comparison with other boranes. The marked decomposition of $B_{10}H_{14}$ is observed only above 170°. Decaborane does not react with the oxygen of the air at room temperature, and it still does not react at 60°, but the spontaneous ignition of $B_{10}H_{14}$ takes place at 100°. At room temperature, decaborane hydrolyzes with water very slowly, while it hydrolyzes very rapidly in the case of boiling. Decaborane is readily soluble in alcohol, ether, and benzene.

TABLE 64

Lower Limit of Explosion of the B_5H_9-O_2 System in a Spherical Quartz Vessel at Room Temperature [34]

1 Диаметр сосуда, см	3,7	6,62
2 Давление B₅H₉, мм рт. ст.	0,77 0,83 4;45 4,36 1,00 1,74 1,57	1,03 1,01 1,98 1,94 2,98 3,01 4,02 4,08
3 Давление O₂, мм рт. ст.	2,9 2,8 1,9 2,1 2,7 2,2 2,4	1,51 1,66 1,32 1,33 1,18 1,25 1.31 1,19
4 Результат*	+ − − + − − −	− + − + − + − +

*+ explosion occurred; − explosion did not occur.

1) Vessel diameter, cm; 2) B_5H_9 pressure, mm Hg;

3) O_2 pressure, mm Hg; 4) result*.

At the present time, the most convenient method of obtaining boranes is the direct reduction of boron chloride, boron bromide, or boron fluoride with hydrogen in the presence of granulated aluminum or other metals which bind chlorine or bromine [35-37].

The diborane-formation reaction follows the equation

$$2BCl_3 + 3H_2 + Al \rightarrow B_2H_6 + 2AlCl_3.$$

This method is used to pass, at temperatures of 320-500°, vapors of boron chloride with hydrogen, in a molecular relationship of $BCl_3 : H_2 = 1:3$, through a heated reaction column filled with granulated aluminum. The products of the reaction condense in receivers.

Boron chloride does not enter completely into the reaction. Depending on the conditions of the reaction, the conversion ratio for the boron chloride attains 6-30%, and there are from 3 to 17% B_2H_6 in the condensed products.

Boron chloride is obtained by the chlorination of a mixture of borates with carbon:

$$Na_2B_4O_7 + 2Cl_2 + 7C \rightarrow 4BCl_3 + 7CO + 2NaCl.$$
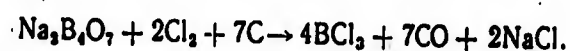
This method is used by industry in the USA.

Plans are underway for the industrial production of B_2H_6 in the USA by the following method:

$$6LiH + 2(C_2H_5)_2O \cdot BF_3 \rightarrow B_2H_6 + 6LiF + 2(C_2H_5)_2O$$
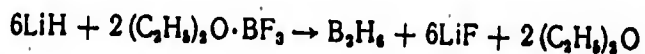
in addition to the derivation of B_2H_6 through boron chloride.

Sodium borohydride is also used for the reduction of boron fluoride; in this case, a yield of 88% is attained. Sodium borohydride is obtained on an industrial scale and serves as a source of hydrogen for balloons and for the torpedoes used by the submarine fleet.

Borohydride is obtained from boron fluoride and sodium hydride through the following reaction:

$$4NaH + BF_3 \cdot O(C_2H_5)_2 \rightarrow NaBH_4 + 3NaF.$$
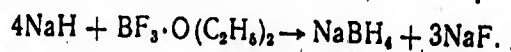
As sodium borohydride reacts with boron-fluoride etherate, diborane is formed with 98% yield:

$$3NaBH_4 + 4(C_2H_5)_2O \cdot BF_3 \rightarrow 2B_2H_6 + 3NaBF_4 + 4(C_2H_5)_2O.$$
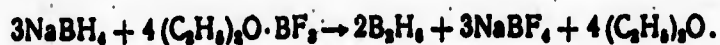
Boron fluoride, which serves as a source for the diborane, is produced industrially from borax and hydrogen fluoride through the following reaction:

$$Na_2B_4O_7 \cdot 10H_2O + 12HF \rightarrow Na_2O \cdot 4BF_3 + 16H_2O$$
$$Na_2O \cdot 4BF_3 + H_2SO_4 \rightarrow 4BF_3 + Na_2SO_4 + H_2O.$$
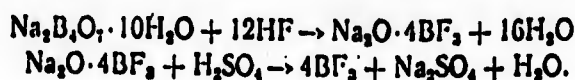
Diborane can also be obtained on the basis of the general equation:

$$Al + 4\tfrac{1}{2}H_2 + BF_3 + 3C_2H_4 \rightarrow AlF_3 + 3C_2H_6 + \tfrac{1}{2}B_2H_6.$$
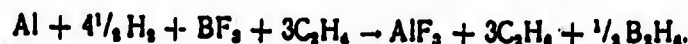
This method involves several stages:

$$Al + 3C_2H_4 + 1\tfrac{1}{2}H_2 \rightarrow Al(C_2H_5)_3$$
$$Al(C_2H_5)_3 + BF_3 \rightarrow B(C_2H_5)_3 + AlF_3$$
$$2B(C_2H_5)_3 + 3H_2 \longrightarrow B_2H_6 + 6C_2H_6.$$
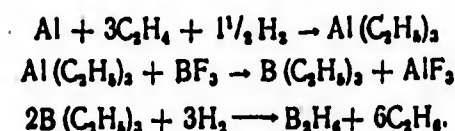
Diborane is a material which yields other boranes in pyrolysis. The pyrolysis is carried out at a temperature of 175-250° and at a pressure of 102-106 mm Hg, and the diborane is in contact with the heated reactor for periods of 2.7 to 3.3 seconds, in continuous-flow apparatus. The process can be described by the following equation [38]:

$$B_2H_6 \rightleftarrows 2BH_3 \xrightarrow{2B_2H_6} 2B_3H_7(+2H_2) \xrightarrow{2B_2H_6}$$
$$2B_4H_8 + 2H_2$$
$$\nearrow$$
$$\rightarrow 2B_5H_{11}(+2H_2) \bigg\langle$$
$$\searrow$$
$$B_2H_6 + \text{higher hydrides}$$
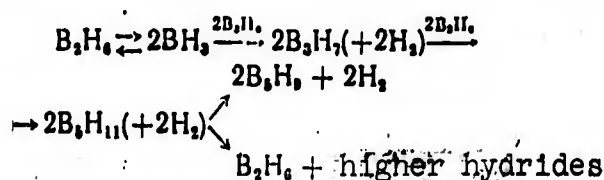
The best yield (up to 80%) of stable pentaborane B_5H_9 is attained at a temperature of 225°. A high diborane conversion ratio is attained at this temperature as well. The product of the reaction contains approximately 85% pentaborane B_5H_9 and 15% solid borane. The maximum decaborane yield may be attained at 120° and amounts to 60% of the diborane which entered into the reaction.

An increase in the temperature of reaction to 250° enhances an in-

crease in the yield of solid boranes to 30 to 50% [38]. Of the boron compounds containing hydrogen and nitrogen in addition to the boron, we should mention borazole.

Borazole $B_3N_3H_6$ is obtained [20] through the heating of diborane diammoniate or tetraborane diammoniate in a closed vessel at 180-190°:

$$3B_2H_6 \cdot 2NH_3 \rightarrow 2B_3N_3H_6 + 12H_2.$$

A new method for the derivation of $B_3N_3H_6$ from lithium borohydride and ammonium chloride, through the following reaction [39], has recently been proposed:

$$LiBH_4 + 3NH_4Cl \rightarrow B_3N_3H_6 + LiCl + 9H_2.$$

In this case it is not necessary to synthesize the boranes in advance. The reaction takes place between a mixture of reagent powders ($LiBH_4$ and NH_4Cl) at a temperature of around 300°, with a yield of 25-35% $B_3N_3H_6$.

Borazole is not a substance exhibiting high heating value (its heating value is around 7800 kcal/kg), but it may apparently be of interest as an initiator of combustion.

More detailed information on compounds of boron with hydrogen and nitrogen are presented in the article by A.F. Zhigach and L.N. Kochnev, entitled "Azotosoderzhashchiye proizvodnyye diborana" ["Nitrogen-Bearing Derivatives of Diborane"] [40]. Aluminum borohydride is used as an additive for air-reaction engine fuels to ignite these fuels under high-altitude conditions; it is obtained in accordance with the following equation:

$$Al(C_2H_5)_3 + 3B_2H_6 \rightarrow 2Al(BH_4)_3 + 3B(C_2H_5)_3.$$
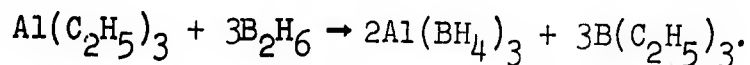
4. Organic Boron Compounds

The heating values of elementary organic compounds of boron and beryllium are somewhat higher than in the case of the hydrocarbons. However, this is observed only for the lower members of the homologous

- 205 -

Properties of Certain Alkyl Derivatives of Boron

1 Название	2 Формула	3 Плотность ρ	4 Т. кип., °C
5 Триметилбор	$B(CH_3)_3$	0,62 (20°)	—20
6 Триэтилбор	$B(C_2H_5)_3$	0,6961 (28°)	90—95
7 Три-н. пропилбор	$B(C_3H_7)_3$	0,7204 (24,7°)	156
8 Триизопропилбор	$B[CH(CH_3)_2]_3$	—	33—35 (12 мм)
9 Трииизобутилбор	$B[CH_2CH(CH_3)_2]_3$	0,7380 (25°)	186
10 Три-трет. бутилбор . . .	$B[C(CH_3)_3]_3$	—	71 (12 мм)
11 Трииизоамилбор	$B[CH_2CH_2CH(CH_3)_2]_3$	0,7600 (23,4°)	119 (14 мм)
12 Тетраметилдиборэтан . .	$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!>\!\! B-C_2H_4-B\!\!<\!\! \begin{matrix} CH_3 \\ CH_3 \end{matrix}$	—	98

1) Designation; 2) formula; 3) density, ρ; 4) boiling point, $^{\circ}C$; 5) trimethylboron; 6) triethylboron; 7) tri-n. propylboron; 8) triisopropylboron; 9) triisobutylboron; 10) tri-tert. butylboron; 11) triisoamylboron; 12) tetramethyldiboroethane.

series, the higher homologs already differing little in terms of heating value.

A simple and convenient method of obtaining trialkyl derivatives of boron involves the reaction of boron halides or the etherate of boron fluoride with magnesium-organic compounds:

$$3RMgX + (C_2H_5)_2O \cdot BF_3 \rightarrow (R)_3B + 3MgFX.$$
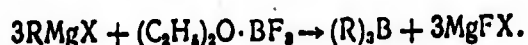
This method, which results in a high yield of around 70-80%, yields triethyl-tri-n. propyl-, triisopropyl-, triisobutyl-, tri-tert. butyl-, and triisoamyl-boron [41].

Some properties of alkyl derivatives of boron are presented in Table 65.

The Grignard reaction can be carried out with boron fluoride, boron chloride, and boron bromide; however, the most readily accessible is boron fluoride in the form of a gas or an etherate.

Boron fluoride is an industrial product and can be obtained through the following reaction:

$$3CaF_2 + B_2O_3 + 6H_2SO_4 \rightarrow 2BF_3 + 3Ca(HSO_4)_2 + 3H_2O,$$
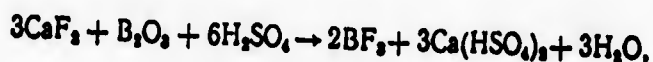
as well as by other methods [42].

Boron-organic compounds can also be obtained by the direct reaction of diborane with olefins through the following reaction:

$$B_2H_6 + 6C_nH'_{2n} \rightarrow 2B(C_nH_{2n+1})_3.$$
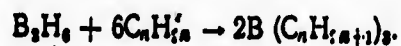
For example, on heating isobutylene together with diborane at 100°, tert. butylboron is obtained, and this has a boiling point of 181.5° [43].

Boron-organic compounds with two boron atoms per molecule were obtained in 1954 from diborotetrachloride through the following reaction [44]:

$$B_2Cl_4 + CH_2 = CH_2 \rightarrow Cl_2B - CH_2 - CH_2 - BCl_2.$$
$$Cl_2B - CH_2 - CH_2 - BCl_2 + 2Zn(CH_3)_6 \rightarrow$$
$$\rightarrow (CH_3)_2B - CH_2 - CH_2 - B(CH_3)_2 + 2ZnCl_2.$$
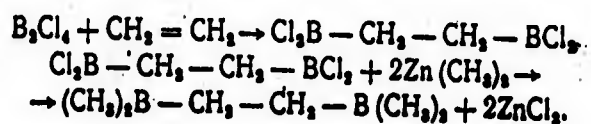
By analysis, the tetramethyldiboroethane contains 19.98% boron, and this substance is not too stable.

Trimethyl- and triethyl-boron ignite easily and spontaneously in air, the higher homologs can ignite spontaneously, but first of all they absorb the oxygen of the air with pronounced heating and they fume in air. The boron organic compounds are comparatively stable in water and acids, but are easily decomposed by alkalis.

5. Heating Value and Hypothetical Efficiency of Fuels Based on Boron and Beryllium

In considering the heating values of boron, beryllium, aluminum, and their compounds, we should take into consideration the aggregate state of the oxides, since a certain quantity of heat is exr nded on the melting and vaporization of the oxides. In certain cases, this quantity of heat may even exceed the heat of the oxide formation. The state of the oxide is also a function of the temperature at which the combustion process takes place.

Below we present the melting and boiling points [45, 46] of the corresponding oxides:

	M.p., °C	B.p., °C
Al_2O_3	2050	2250
B_2O_3	557	1700
BeO	2570	3900
Li_2O	—	1700
MgO	2800	3600

If we take into consideration the need to cool air-reaction engines and if we also consider the fact that there will be an excess of air over the theoretical quantity, the temperature of the exhaust gases will hardly exceed 1000-1500°. Therefore, all of the metal oxides will be in the solid state, and the boron oxide will be in the liquid state. The latent heat of fusion for the boron oxide is approximately 6-8 kcal/g·mole and, therefore, in calculating the heating value which may be attained in an engine, the latent heat of fusion must be subtracted from the heat of the formation of the solid boron oxide. The heating values of boron, beryllium, and their compounds, are presented in Table 66.

According to literature data [44], the highest heat of combustion for B_2H_6 is 17,800; for B_5H_9 it is 16,700; for $B_2H_5CH_3$, 13,900; for $B_2H_5C_2H_5$, 13,600; for $B_2H_2(C_2H_5)_4$, 11,700; and for BeH_2, 18,000 kcal/kg.

Apparently, the most suitable among the high heating-value compounds are the hydrocarbons — pentaborane and decaborane. The former could be used in hydrocarbon solutions, and the latter in the form of suspensions. Boron-organic compounds with a single boron atom per molecule, apparently, are of no interest, since trimethylboron is a gas, and the liquid compounds have a heating value not in excess of 11,000 kcal/kg, i.e., liquid boron-organic compounds differ little from the hydrocarbons with respect to heating value. They probably could be used as combustion initiators under specific conditions.

TABLE 66

Weight and Volume Heating Value of Boron, Beryllium, and Their Compounds

1 Вещество	2 Символ, формула	3 Плот-ность	4 Т. пл., °C	5 Т. кип., °C	6 Теплотворная способность * Q_H	
					7 ккал/кз	8 ккал/л
9 Бор	B	2,3	Тв. [22]	—	13 670	31 400
10 Бериллий	Be	1,81	Тв.	—	15 000	27 800
11 Пентаборан . . .	B_5H_9	0,63	—46,6	58	16 183	9 630
12 Декаборан	$B_{10}H_{14}$	0,92	+99	—	16 110	14 100
13 Боргидрид алюминия	$Al(BH_4)_3$	0,56	—65,4	44,5	13 750	7 670
14 Боргидрид бериллия	$Be(BH_4)_2$	—	+31	91,3	16 100	—
15 Боргидрид лития.	$LiBH_4$	0,67	273	При нагревании разлагается	14 300	9 500
16 Диметилбериллий	$Be(CH_3)_2$	—	Тв. [23]	—	12 700 (11 900)	—
17 Триметилбор . .	$B(CH_3)_3$	0,62	—	—20	11 900	8 900
18 Триэтилбор . . .	$B(C_2H_5)_3$	0,69	—	90—96	11 200	—
19 Трипропилбор . .	$B(C_3H_7)_3$	0,72	—	156	10 700	—
20 Триметилалюминий	$Al(CH_3)_3$	0,73	+15	125	10 550	—
21 Тетраметилдибороэтан	CH_3 $\rangle B—C_2H_4—B\langle$ CH_3 (CH_3) (CH_3)	—	—	98	11 800	—

*In calculating the heat of combustion, the boron oxide is assumed to be in the liquid state (the heat of formation for liquid B_2O_3 is 295 kcal/mole),

the oxides of aluminum and beryllium are assumed to be in the solid state, and the water is assumed to be in the form of vapor. The heat of formation for the boranes is assumed to be equal to 0. For the heat of formation of the elementary organic compounds: dimethylberyllium, the heat of formation for ethane has been selected; for trimethylboron, the heat of formation for $1^1/2$ ethane molecules has been chosen.

1) Substance; 2) symbol, formula; 3) density; 4) melting point, °C; 5) boiling point, °C; 6) heating value, Q_H; 7) kcal/kg; 8) kcal/liter; 9) boron; 10) beryllium; 11) pentaborane; 12) decaborane; 13) aluminum borohydride; 14) beryllium borohydride; 15) lithium borohydride; 16) dimethylberyllium; 17) trimethylboron; 18) triethylboron; 19) tripropylboron; 20) trimethylaluminum; 21) tetramethyldiboroethane; 22) solid; 23) decomposes on heating.

Alkyl derivatives of borane are used in reaction engineering and in the USA these fuels carry the following designations: HEF-1, HEF-2, and HEF-3 [46a, 46b].

The HEF-2 propellant is ethyldecaborane, which has a density of 0.82 and a heating value of 14,000 kcal/kg. The propellant can withstand heating to 260° for 60 seconds.

Alkyl boranes are hypergolic in air, and form solid tar products when heated as a result of polycondensation with splitting off of hydrogen. The use of additives makes it possible to retard this process. The cost of alkyl boranes in the USA is estimated at $2000 per ton.*

Borane fuels are toxic. Decaborane results in slow and progressive weakening of heart activity. Inhalation of diborane is injurious primarily to the lungs, whereas the slowly hydrolyzing compounds accumulate in the organism and result in the destruction of the central nervous system, the liver, and the kidneys. The maximum permissible concentration of alkyl borane in the air is $10^{-4}\%$.

We know of extremely stable polymers which contain residue of decaborane and phosphorus, and these are stable below 550°; in addition, we know of high-molecule polymers of boron having the following composition $(BCH_2)_x$ and $(-B-CH_2-CH_2-B-)_x$, as well as boron-nitrogen-bearing polymers of the following structure:

$$\ldots BH_2-NH_2 \ldots BH_2-NH_2 \ldots BH_2-NH_2 \ldots,$$
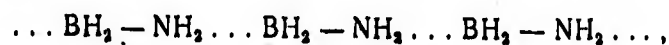
which form on the heating of diborane ammoniate $B_2H_6 \cdot 2NH_3$ [47].

6. Effect of Heating Value and Fuel Density on Flight Range

The flight range S which is attainable with various fuels is the most complete characteristic of fuel quality.

This quantity is a function of specific fuel consumption (C_{ud}), of fuel density (ρ), the fuel reserve $(\rho \cdot w)$ on board the aircraft, and

the weight (G_0) of the aircraft without fuel:

$$S = k\frac{3.6 \cdot v}{C_{yx}} \ln \frac{G_0 + \rho \cdot w}{G_0}, \qquad (a)$$

where $\underline{k}$ is a coefficient; $\underline{v}$ is the flight velocity; and $\underline{w}$ is the volume of the tanks (see Chapter 1).

The specific fuel consumption, i.e., the fuel flow rate (in kg) in one hour for the development of 1 kg of thrust is a function of the heating value and, therefore, given the characteristic of fuel quality the problem can be reduced to an evaluation of the specific fuel consumption which is determined by the following formula:

$$C_{yx} = \frac{3600\, g_r}{\frac{1}{g}\left\{ \sqrt{2g\,427\,\eta_i\eta_g \frac{Q_n}{aL_0} + v^2} - v \right\}}, \qquad (b)$$

where Q_H is the heating value; α is the excess-air ratio; L_0 is the quantity of air (in kg) needed to burn 1 kg of fuel; g_t is the weight ratio of the fuel to the air passing through the engine.

On the basis of the conditions required for the operation of air-reaction engines, the gas temperature in front of the turbine must maintain a constant value regardless of the fuels employed.

In this case, the rise in the gas temperature as a result of fuel combustion must also maintain a constant value:

$$t = \frac{1}{C_p} \cdot \frac{Q}{aL_0} = \text{const}, \qquad (c)$$

where C_p is the heat capacity of the gases.

With fuels of various heating values this is possible only by changing the excess-air ratio α. With great values of α, the heat capacity of the gases in front of the turbine is virtually independent of the composition of the products of combustion; therefore, the ratio

$$Q/\alpha L_0 = \text{const} \qquad (d)$$

must be a quantity that is constant for various fuels.

Under these conditions, the specific fuel consumption will change

only as a result of the following quantity:

$$g_t = 1/\alpha L_0.$$

The quantity of air required for the combustion of 1 kg of fuel is determined from the equation of combustion; α is determined as a function of the given temperature in front of the turbine, in accordance with Eqs. (c) or (d).

Let us determine these quantities as an example for three fuels: a fuel of the kerosene type (T-1), methylnaphthalene, and pentaborane.

A fuel of the kerosene type has an elementary composition as follows: C, 86.42%; H, 13.38%; the conventional formula is $C_{7,2}H_{13,38}$ or $C_nH_{1,9n}$.

The equation of combustion for such a fuel, in atmospheric air, can be presented in the following form:

$$C_nH_{1,9n} + 1,475O_2 + n\,5,54N_2 \rightarrow nCO_2 + n\,0,95H_2O + n\,5,54N_2$$
$$L_0 = \frac{(1,475 \cdot 32 + 5,54 \cdot 28) \cdot n}{n \cdot 13,9} = 14,6 \text{ kg of air/kg of fuel.}$$

Let us assume that $\alpha = 4$; in this case, the increase in temperature as a result of the combustion of the fuel has the following value:

$$\Delta t = \frac{1}{C_p}\,\frac{Q}{\alpha L_0} = \frac{0 \cdot 10\,250}{0,245 \cdot 4 \cdot 14,6} = 715°.$$

TABLE 67

Certain Characteristics of Fuels of Various Composition*

1 Топливо	2 Формула	ρ_4^{20}	Q_H	α	g_T	L_0	c_{yA}
3 Керосин (T-1)	$C_nH_{1,9n}$	0,820	10 250	4,00	1:58,2	14,6	1,44
4 Метилнафталин.	$C_{11}H_{10}$	1,025	9 394	4,15	1:53,8	13,0	1,55
5 Пентаборан	B_6H_9	0,630	15 340	6,06	1:79,5	13,1	0,95
6 Бор.	B	2,300	13 670	8,25	1:78,5	9,5	1,06

*Denotations as in Chapter 1.

1) Propellant (fuel); 2) formula; 3) kerosene (T-1);
4) methylnaphthalene; 5) pentaborane; 6) boron.

The actual gas temperature in front of the turbine will be higher

as the result of the heating of the air produced by compression.

The ratio of air to fuel is the following:

$$g_r = \frac{1}{\alpha L_0} = \frac{1}{4 \cdot 14.6} = \frac{1}{58.2} .$$

The heat content (enthalpy) of the gases is:

$$q = Q/\alpha L_0 = 175.6 \text{ kcal/kg of air.}$$

For the remaining fuels L_0 is found on the basis of the reaction
equation, and α is determined from the following ratio:

$$\alpha = \frac{Q}{175.6 \cdot L_0} .$$

For an aromatic hydrocarbon — methylnaphthalene — and a compound
of boron with hydrogen — pentaborane — the combustion reactions may be
written in the following form:

$$C_{11}H_{10} + 13.5O_2 + 50.7N_2 \rightarrow 11CO_2 + 5H_2O + 50.7N_2$$

$$(L_0 = 13.50 \text{ kg/kg}, \ \alpha = 4.15)$$

$$B_5H_9 + 6O_2 + 22.6N_2 \rightarrow 2.5B_2O_3 + 4.5H_2O + 36.8N_2$$
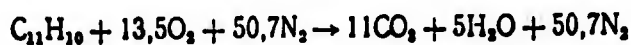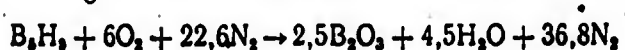
$$(L_0 = 13.1 \text{ kg/kg}, \ \alpha = 6.67)$$

The values of a number of parameters for several types of fuels
of various composition are presented in Table 67.

The excess-air ratio is somewhat greater for aromatic fuels than
in the case of paraffinic-naphthenic fuels, and the quantity of air
required for the combustion of the boron is even lower.

In the case of boron-bearing fuels, the excess-air ratio increases
substantially as a result of the heating value, and there is a corres-
ponding increase in the product αL_0 in order to preserve a constant gas
temperature at a high value of Q_H. Thus the specific fuel consumption
is a function of the heating value and the stoichiometric coefficients
in the equation of combustion.

Table 68 presents the change in flight range as a function of
heating value and density for an aircraft exhibiting a weight of $G_0 =$

TABLE 68

Change in Flight Range as a Function of Heating
Value and Fuel Density [1, 3]

1 Топливо	2 Плотность	3 Теплотворная способность $Q_{н}$, ккал/кг	4 Запас тепловой энергии в баках, ккал	5 Удельный расход $C_{уд}$	6 Дальность полета, км
7 *Углеводородные топлива*					
8 Авиационный керосин	0,82	10 250	$1,05 \cdot 10^{9}$	1,44	15 000
9 Авиационное топливо широкого фракционного состава	0,76	10 350	$0,985 \cdot 10^{9}$	—	14 500
10 Декалин (цис)	0,89	10 225	$1,15 \cdot 10^{9}$	1,44	15 900
11 Тетралин	0,97	9 723	$1,18 \cdot 10^{9}$	1,51	15 900
12 Метилнафталин	1,02	9 394	$1,18 \cdot 10^{9}$	1,55	16 000
13 Декан	0,73	10 573	$0,97 \cdot 10^{9}$	1,39	14 500
14 *Неуглеводородные топлива*					
15 Пентаборан	0,63	15 340	$1,27 \cdot 10^{6}$	0,95	19 000
16 Бор	2,3	13 670	$3,02 \cdot 10^{9}$	1,06	(35 000)*
17 Бериллий	1,85	15 000	$3,46 \cdot 10^{9}$	0,98	(23 700)*
18 Алюминий	2,7	7 290	$2,46 \cdot 10^{9}$	2,0	(19 800)*
19 Углерод	2,0	7 840	$1,96 \cdot 10^{9}$	1,88	(18 900)*
20 *Смеси топлива*					
21 Керосин — 70% 22 Бор — 30%	1,01	11 360	$1,40 \cdot 10^{9}$	1,33	18 500
23 Тетралин — 60% 24 Алюминий — 40%	1,33	8 620	$1,43 \cdot 10^{9}$	1,68	17 500
25 Керосин — 70% 26 Пентаборан — 30%	0,74	11 800	$1,00 \cdot 10^{9}$	1,28	16 000
27 Метилнафталин — 70% 28 Пентаборан — 30%	0,85	11 200	$1,10 \cdot 10^{9}$	1,37	16 500

*The practical range, with fuels exhibiting a density of 1.5-2.5, will be lower because of the increased weight of the aircraft for reasons of strength.

1) Propellant (fuel); 2) density; 3) heating value Q_{H}, kcal/kg; 4) reserve of thermal energy in tanks, kcal; 5) specific fuel consumption, C_{ud}; 6) flight range, km; 7) hydrocarbon fuels; 8) aviation kerosene; 9) aviation fuel of wide fractional composition; 10) decalin (cis); 11) tetralin; 12) methylnaphthalene; 13) decane; 14) nonhydrocarbon fuels; 15) pentaborane; 16) boron; 17) beryllium; 18) aluminum; 19) carbon; 20) fuel mixtures; 21) kerosene — 70%; 22) boron — 30%; 23) tetralin — 60%; 24) aluminum — 40%; 25) kerosene — 70%; 26) pentaborane — 30%; 27) methylnaphthalene — 70%; 28) pentaborane — 30%.

= 58 tons and a fuel-tank capacity (volume) of $w = 125 \text{ m}^3$. It is assumed in this case that the flight range with aviation kerosene is equal to 15,000 km, and the weight of the aircraft does not undergo any change in the transition from kerosene to heavier fuels (propellants).

Theoretically (without taking into consideration any possible increase in the weight of the aircraft) an increase of approximately 1000 km in range can be achieved by heavy propellants of the bicyclic naphthenic and aromatic hydrocarbon type. In the practical solution of this problem, the possible increase in aircraft weight as a result of strength requirements should also be taken into consideration. Range is substantially increased with boron-bearing fuels, since the specific fuel consumption is reduced.

7. Methods of Obtaining Fuel Suspensions with Additives Exhibiting High Heating Values

a) General data

One of the methods used to obtain fuels exhibiting high heating values may involve the preparation of suspensions or colloidal solutions of boron, beryllium, and similar substances in petroleum products [46a].

For colloidal solutions, solid particles with dimensions of $1 \cdot 10^{-5}$ to $1 \cdot 10^{-7}$ cm must be dispersed in the hydrocarbon medium. In this case, the dispersed substance and the dispersion medium make up the colloidal system as a single whole. Such colloidal systems are referred to as metal sols. For example, in sols of platinum and gold there are metal particles having dimensions of the order of $5 \cdot 10^{-7}$ cm.

However, the production of such colloidal solutions of high concentration is a difficult problem; it is therefore simpler to prepare suspensions of metal powders in hydrocarbons; the powders are prevented

from settling by increasing the viscosity of the medium. In this case, comparatively coarsely dispersed solid particles with dimensions of 0.05-0.1 mm (aluminum powder) or 0.0005-0.020 mm (fine aluminum and beryllium powder) are not directly parts of the colloidal system, but serve as fillers for the colloidal solution.

To increase the viscosity of the medium, high-molecular substances or salts of fatty or similar organic acids are dissolved in hydrocarbons, and this produces colloidal systems with high viscosity. As has already been mentioned, a suspension of magnesium and aluminum in gasoline has been tested in jet engines [3].

A solution of natural and synthetic rubber in petroleum products has been proposed for the stabilization of these suspensions, and polyisobutylene with a molecular weight of 20,000 to 40,000 has also been proposed for this purpose. The solution of high-molecular substances, even in small quantities (2-5%), calls for extensive heating and good mixing. In this manner viscous solutions are obtained, and these contain solid powders for several hours or days, at the end of which time deposition begins. A partially stratified suspension can be regenerated by subsequent mixing [1].

Wax and paraffin are used to thicken petroleum products; however, in this case it is necessary to introduce a large quantity of such additives (20-30%) in order to attain the required consistency.

Thickened (jellied) viscous petroleum products are used for flame throwers and weapon charges. In the first case, in order to increase the range of the flame, and in the second case to prolong the combustion time for the fuel (combustible) used as the ignitor [47]. Thickened or solidified (jellied) petroleum products in this case are produced with the salts of high molecular fatty acids.

Jellied kerosene for incendiary weapons is produced in the follow-

ing manner. During heating, 2-3% stearin, representing a mixture of stearic ($C_{17}H_{35}COOH$) and palmitic ($C_{15}H_{31}COOH$) acids, is dissolved in the kerosene. At 75-80° and with vigorous mixing, caustic soda in an alcohol solution, in a quantity equivalent to the acid, is added to the solution. In this case, sodium stearate is formed:

$$C_{17}H_{35}COOH + NaOH \rightarrow C_{17}H_{35}COONa + H_2O.$$
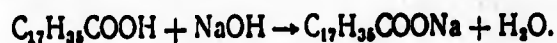
Palmitic acid reacts in an analogous way.

Sodium stearate in kerosene or gasoline, at a temperature of 75-80°, forms a true solution. However, when cooled to 50-60°, the true solution passes into a state of colloidal solution with the formation of a sol, subsequently a gel, and the entire system is converted into a semihard inviscid mass that is characteristic of jellies [48]. Thickened (jellied) petroleum products are stable in storage and they do not flow under the action of gravity, but can be carried through tubing under pressure. The uniform structure of a jellied fuel (combustible) is destroyed by mixing or grinding, but it can later be restored to some extent.

Soap gels can also be obtained in hydrocarbons through the solution of hard soaps (salts of high molecular organic acids) in hydrocarbons by heating or even at normal temperature.

Calcium, aluminum, and magnesium soaps have poorer thickening properties than sodium soaps. At the same time, the nature of the thickening by means of salts of multivalent metals such as, for example, aluminum, are different than in the case of sodium salts. Aluminum soaps form viscous, sticky, and free-flowing systems which exhibit the property of restoring well their initial structure; sodium soaps form jellies in hydrocarbons, and the structure of these jellies is easily destroyed.

The thickening of oil fractions is widely used for the preparation

of consistent lubricants and this is discussed in the appropriate courses [48].

In the USA, a gasoline-based jellied combustible (fuel) is identified as "napalm." For the production of napalm, from 4 to 11% of a thickening powder is dissolved in gasoline; this powder is apparently a mixture of aluminum salts of oleic and naphthenic acids and the acids that enter into the composition of coke oil. Aluminum salts of organic acids are obtained by the reversible reaction between the sodium salts of acids and aluminum sulfate. The outstanding features of napalm are its considerable viscosity and adhesion, which make it suitable for use in flame throwers and as charges for incendiary weapons [49].

To increase the efficiency (combustion temperature) of jellied combustibles, a 50-60% magnesium powder, which does not settle out despite the high viscosity of the medium, is sometimes introduced into these jellied combustibles as an ignitor [47].

b) Theoretical premises for preparation of suspensions [50]

Rate of particle deposition. In the preparation of stable suspensions, the deposition of the dispersed particles must be avoided.

The rate of deposition for solid particles having a radius r and a density ρ in a medium of density D and viscosity η is expressed by the following equation, in accordance with the Stokes law:

$$v = \frac{2}{9} g \frac{r^2 (D - \rho)}{\eta} .$$

The Stokes law follows from the relationship between the resistance force, i.e., the friction force, that is produced on the motion of spherical particles at a constant velocity in a medium having a definite viscosity, and the force of gravity acting on the particle. As the particle falls at a constant velocity, the force of friction

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offsets the force of gravity.

The Stokes law is valid for particles of true spherical shape and for a medium having a true viscosity rather than a structural viscosity which changes in value as a function of the applied force as is the case in colloidal systems. In true suspensions there are particles that are not spherical in shape. However, the Stokes law may be used, with certain allowances, for the characteristics of the stability or true metal suspensions in jellied petroleum products.

It follows from the Stokes equation that the rate of particle deposition can be reduced and, consequently, suspension stability increased by the following steps:

1) increasing the viscosity of the medium in which the solid particles are dispersed;

2) reducing the dispersed particles in size;

3) increasing the density of the medium;

4) during the grinding of the substance to be dispersed, the dispersion in a liquid medium can be improved by the introduction of surface-active substances into the medium.

The physicochemical nature of jellied combustibles. As petroleum combustibles are thickened in order to attain the required viscosity of the medium, a colloidal system is formed. The thickening takes place through the solution of high-molecular substances or the salts of high-molecular fatty acids in hydrocarbons, with the resultant formation of colloidal systems that are referred to as sols or gels, depending on their nature. These systems are characterized, unlike true solutions, as structured systems resulting from the interaction of dissolved solvated particles (macromolecules) as a result of their high molecular weight, producing grids or cells containing the solvent. As a result the viscosity of the solution increases sharply in comparison

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to the initial solvent. Such solutions in hydrocarbons are referred to as lyophilic sols.

The viscosity of lyophilic sols is a function of the concentration of the dispersed phase (dissolved substance) and temperature. With high concentrations of dissolved substance, an ever increasing vigorous interaction between the macromolecules sets in and the viscosity increases sharply. With a change in temperature, the effective length of the macromolecules changes, as does the degree of their solvation by the solvent, and this results in a pronounced change in viscosity with temperature.

With increased concentration of the dispersed phase or with a drop in temperature, gelatinization of the system takes place.

Gelatinization is that process which results in the formation of a jelly or gels of sols. With the gelatinization of the sol, the microscopic divisions disappear and the entire mass of the sol solidifies into a homogeneous jelly that resembles a semisolid, since the fluidity, characteristic of liquids, disappears. At the same time, the sol preserves its fluidity, even in the case of high viscosity.

The gelatinization process consists in the combination of individual colloidal particles into loosely structured aggregates under the action of attraction forces. These aggregates form grids whose cells contain the dispersion medium.

The hardness of the formed jelly is directly proportional to the concentration of the initial solution. Some conditional temperature at which the system, in a tube, does not deform as the tube is inclined, is selected as the thickening (gelatinization) temperature. There is also a definite temperature at which the jelly makes the transition into a sol, and this temperature is assumed to be the melting point of the gel-jelly.

The jelly can be brought to the state of a sol by mixing or by similar mechanical action. This is referred to as the thixotropic destruction of jelly. In a state of rest, such a sol again gelatinizes. The formation of thixotropic gel can be explained by the appearance of a mutual bond between the particles which form the elements of the jelly structure, said jelly easily destroyed through mechanical action.

As a result of this phenomenon, jellies do not flow and they are not transported under the action of gravity, nor can there be any mixing of particles dispersed in them, i.e., the particles do not settle out.

However, under the action of an external force, i.e., in the case of a pressure difference, such jellies become fluid, since they have made the transition to the sol state.

The viscosity of jellied combustibles. In the utilization of jellied combustibles containing fillers, an important problem is the fluidity of the jellies, which must differ from the initial solvent as little as possible. High viscosity may make it difficult to pump and vaporize a combustible of this type during ignition. On the other hand, with low viscosity the dispersed powders might settle out.

Viscosity is characterized by the resistance of a body to a relative shift of 1 cm^2 per second of the parallel layers of disperse powders. The viscosity of normal liquids is determined experimentally by the discharge of a liquid through a fine capillary tube (viscosimeter) according to the following equation:

$$\eta = K \cdot P \cdot \tau,$$

where η is the viscosity; K is the viscosimeter constant; P is pressure; and τ is the discharge time.

The viscosity of ideal liquids is not a function of the applied pressure, nor of the length and radius of the capillary tube of the

viscosimeter.

However, the viscosity of colloidal systems — sols — is a function of the applied force under which the deformation of the sol and discharge take place, since the aggregates of the macromolecules of the colloidal system, their dimensions, and the macromolecules themselves are sensitive to external mechanical action, and are destroyed under the influence of mechanical action; consequently, viscosity also changes. In a state of rest, combinations are formed — the macromolecules become entangled and large aggregates are formed, with the latter resulting in increased viscosity. In the case of mechanical mixing and the rapid shifting of the system, the weakly bonded aggregates are destroyed and dispersed, thus reducing viscosity. This effect of the change in the viscosity of a colloidal system in the case of mechanical action is referred to as "structural viscosity."

The concept of relative viscosity η, determined in the following manner, is taken as the characteristic of viscosity for colloidal systems:

$$\eta = \frac{{}^l\eta_1 - \eta_0}{\eta_0},$$

where η_1 is the viscosity of the solution; η_0 is the viscosity of the solvent.

The structural, or apparent, viscosity is a function of the applied force characterized by a shear stress:

$$f = \frac{P \cdot r}{2l},$$

where f is the shear stress; P is the pressure at which the colloidal system begins to flow; r is the radius of the capillary tube; l is the length of the capillary tube from which the discharge takes place.

Thus the apparent viscosity is a function of shear stress:

$$\lg \eta = a - b \lg f$$

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or

$$\lg \eta = a - k \lg P$$

at constant values for $\underline{r}$ and $\underline{l}$.

The change in the viscosity of the gels, i.e., of the jellies, is an even greater function of the applied pressure than in the case of sols. This is associated with the fact that on the application of small forces, the viscosity of the jelly is infinite, whereas with an increase in the pressure difference flow begins and the gel is converted from a jelly into a sol which exhibits low viscosity.

Thus the relative viscosity of lyophilic hydrocarbon sols and jellies is a function of this pressure difference and can gradually approach the viscosity of the solvent as the pressure difference increases.

The addition of metal powders, for example, to colloidal systems increases their viscosity in direct proportion to the powder concentration; in particular, the smaller the dimensions of the powder particles, the greater the specific surface.

The stability of suspensions in hydrocarbon sols or jellies. The rate of deposition for suspensions in a liquid medium can be characterized by Stokes law and depends on the viscosity of the medium as well as on the dimensions of the particles.

If this quantitative relationship is valid and applicable to this case, the settling out of the solid particles is unavoidable, although the deposition process may continue for a considerable period of time. In this case, the jellied combustible will be physically unstable. However, the flow of the structured colloidal system or the deposition of the solid particles in this system may begin with a definite shear stress.

In either case, the motion of the medium or of the particles in

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the medium may begin as a certain maximum shear stress is attained, or as a force P, corresponding to this shear stress, is reached.

If the gravity acting on the particle is less than the corresponding maximum shear stress for a lyophilic sol in the case of the free fall of the particle, there will be absolutely no settling of the particle, since the viscosity value at small loads will correspond to infinity.

The shear stress is particularly great in the case of jellies which are semisolid in nature and do not shift under the action of gravity, i.e., under the action of small loads. In accordance with this, powder particles dispersed in a jelly medium cannot shift under the action of gravity. However, the shear stress in the case of hydrocarbon jellies is limited to extremely negligible forces which can only resist the shifting of a substance under the action of gravity, i.e., the stratification of the suspension. On application of loads measured in tens of fractions of an atmosphere, the system begins to flow and it passes from a jelly into a sol. At rest, the sol may again turn into a gel.

For the formation of metal suspensions in hydrocarbons, use can be made of the petroleum-product thickening methods which result in colloidal systems that correspond, in nature, to viscous sols (thickened with rubber, aluminum soaps), or gels-jellies (thickened with sodium soaps).

c) Preparation of suspensions

From 1947 through 1957, investigations were being carried on in the USA on fuel suspensions for jet engines, and the future utilization of such suspensions in ZhRD [liquid rocket engines] operating on fluorine [51] is not excluded.

Fuel suspensions are obtained by the dispersion of fine magnesium

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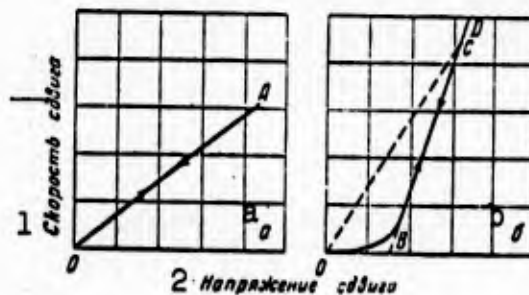
Fig. 59. Behavior of ideal
(Newtonian) fluid and thixo-
tropic system on application
of force. 1) Shear rate; 2)
shear stress.

or boron powders in such aviation kerosenes as JP-3, JP-4, or JP-5, in
quantities up to 50-60%. The stabilization of these powders in the sus-
pended state is achieved by gelatinizing and surface-active additives.
The former include soaps or high-molecular compounds; the latter in-
clude alcohols and acids. The quantity of metal which can be in sus-
pension, and its properties, are determined by the shape and the dimen-
sions of the particles, their dimensional distribution, and the compo-
sition of the hydrocarbon medium.

Fuel suspensions do not have the properties of Newtonian fluids,
i.e., their flow rates are not directly proportional to the acting
force. The physical parameters of these suspensions are determined by
means of viscosimeters of various types. To determine the relationship
between the shear rate or the rotation of the viscosimeter spindle and
the shear stress or the motive force for a wide range of shear rates,
an automatic self-recording viscosimeter was used.

Figure 59 shows graphs which indicate the various types of flows,
and the a graph is for a Newtonian fluid, and the b graph shows the
properties of suspensions. The arrows indicate that the curves were
initially obtained by the continuous increase of shear stress (ascend-
ing curve), and then by the continuous reduction of the shear stress
(descending curve). The shear rate for the substances exhibiting New-

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tonian properties changes linearly with a change in shear stress, and viscosity is proportional to the inverse of the slope of the curve (curve A). In the case of thixotropic materials, it is necessary to apply a certain force — a shear stress — before the rate of shift becomes a linear function of the shear stress (b). The magnitude of the initial force is determined by the segment formed from the intersection of the extrapolated line segment and the axis of the shear stress. The rate of shear for thixotropic systems increases nonlinearly with shear stress (b). If the shear stress required to produce a given rate of shear diminishes in direct proportion to the duration of its effect, the material is thixotropic. Low apparent viscosity and a low value for the initial shear stress of the suspension facilitate the pumping of this suspension by means of pumps. At the same time, high viscosity, high initial shear stress, and thixotropicity prevent the settling out of the suspended particles as deposits.

Deposition stability is determined from the sedimentation of the particles of the suspension in 50-millimeter graduated cylinders at a temperature of 30°. The degree of sedimentation is expressed by a coefficient that has been determined in the form of a ratio between the height of the sedimentary layer and the initial height of the suspension in the cylinder.

The sedimentation process was also observed in large containers.

The relative lightness from which a deposited suspension could again be brought into a dispersed state was estimated in a number of cases by means of shaking a cylinder with the suspension. In order to study the sedimentation process, the particle shapes, and the process of particle agglomeration, as well as to develop a method of estimating the concentration of metal in the suspension, a study was undertaken of the dielectric properties of boron and magnesium in a suspension in
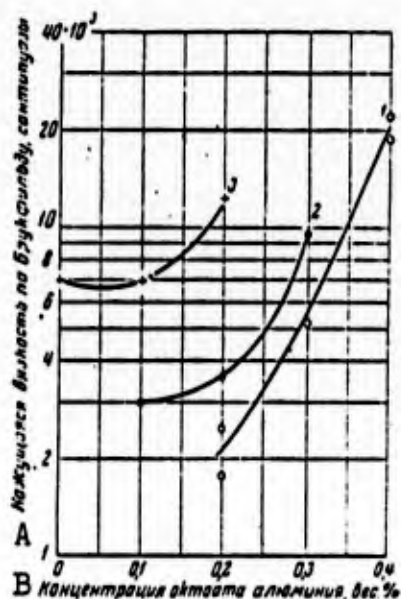
Fig. 60. Viscosity of boron
suspensions of various concen-
trations in aviation kerosene.
1) 50% boron, by weight; 2) 55%
boron, by weight; 3) 60% boron,
by weight; A) apparent viscos-
ity after Brukfil'd [sic], cen-
tipoises; B) concentration of
aluminum octoate, % by weight.

mineral oil.

In the preparation of boron suspensions, use was made of boron
powders that were obtained: 1) by the reduction of boron anhydride with
magnesium or 2) by an electrochemical method.

In the first case, a powder containing from 87 to 91% free boron
with an admixture of boron and magnesium oxide is obtained. The average
particle dimension varies between 0.6 and 1.4 μ; as electron photomic-
rographs show, particles vary in shape. The boron obtained by means of
an electrochemical process contained 97% elementary boron and the av-
erage particle dimension was less than 1 μ.

The suspensions were prepared by the dispersion of a high-disper-
sion boron powder in aviation kerosene with the addition of a gelatin-
izing admixture — aluminum octoate — which is obtained through the in-
teraction of 2-ethylhexanoic acid with aluminum chloride. It is assumed

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that in a number of cases acetylene black, silica aerogel, and a number of bentonites can replace the silica aerogel [sic]. The suspension is prepared at room temperature in the following manner. The thickening reagents are carefully mixed with the hydrocarbon combustibles and then the following metals are introduced into this medium: magnesium, aluminum, or a boron powder. The mixing is carried out by means of a high-speed agitator. To increase the fluidity of the suspension, surface-active additives in quantities from 0.5 to 4.4% are added to the suspension, and the gelatinization additives are included in quantities ranging from 0.2 to 0.4%. The viscosity of the suspension containing 50-60% boron powder changes from 1500 to 100,000 centipoises. Figure 60 shows the effect of additive concentration on apparent viscosity of a boron suspension in aviation kerosene (JP-5); with an increase in the boron concentration above 60%, the viscosity increases to a point at which it becomes difficult to use the suspension.

In the preparation of magnesium suspensions, the work was carried out with a magnesium powder exhibiting particle dimensions of 13-24 μ, and contained more than 94% elementary magnesium; however, these magnesium suspensions do not burn sufficiently well. In this connection, a method was developed for the preparation of finely dispersed magnesium powders, said method based on the cooling of magnesium vapors (magnesium vaporizes at 1090°) with kerosene vapors, and in this case we obtain simultaneously a suspension of pyrophoric magnesium in hydrocarbon. In this case, magnesium particles having dimensions of the order of 0.2 μ are formed.

Storage stability is of outstanding importance from the standpoint of the practical utilization of the suspension.

In the case of suspensions thickened with aluminum octoate, the gel structure of the suspension is impaired during storage.

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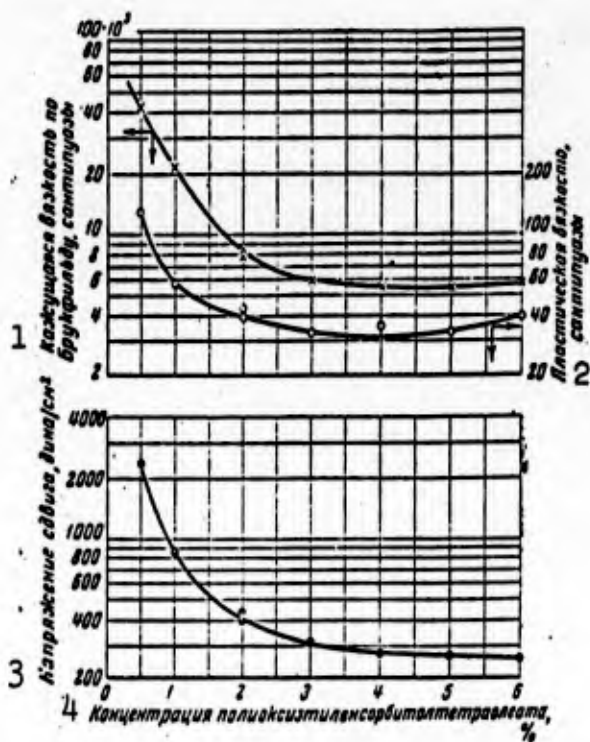
Fig. 61. Change in apparent viscosity
and shear stress as a result of the ad-
dition of a 50%-magnesium suspension of
a surface-active additive. 1) Apparent
viscosity after Brukfil'd [sic], centi-
poises; 2) plastic viscosity, centi-
poises; 3) shear stress, dyn/cm^2; 4)
concentration of polyoxyethylenesorbitol-
tetraoleate, %.

The boron settles out with time, forming a thick deposit which is
not easily dispersed. The destruction of the suspension as a result of
the settling out of the boron or aluminum is accompanied by a drop in
viscosity. The introduction of more than 0.4% aluminum octoate is pos-
sible only if the boron content does not exceed 50%.

The suspension obtained by the vaporization of magnesium yields
systems of high dispersion with an average particle dimension of 2 μ.
With a magnesium content of 50-60%, these suspensions are like inviscid
pastes. In order to obtain a liquid suspension from such a paste, the
suspension must be agitated together with surface-active additives,
and then passed through a colloidal crusher.

It turned out during the investigation of various surface-active

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substances that the most appropriate compounds are those which contain simultaneously the hydroxyl group in combination with the ester or polyoxyethylene group. It is assumed that the effectiveness of these additives can be explained by the fact that they provide for maximum interaction between the hydrocarbon medium and the surface of the dispersed powder.

Figure 61 shows how apparent viscosity and shear stress of a magnesium suspension change with an increase in the content of surface-active additives to 5-6%. Experimental data indicate that suspensions containing 50% magnesium with an average particle dimension of 1.5 μ and 1% of a surface-active additive are quite liquid. Completely usable suspensions, in terms of fluidity, can be prepared in the same way, said suspensions containing 55-60% magnesium. Suspensions prepared in this manner exhibit a tendency to stratification after having been stored for a period of one month.

In using magnesium particles with an average dimension in excess of 4 μ for the preparation of the suspensions, the hydrocarbon medium must be thickened with gelatinizers. Aluminum octoate, in quantities ranging from 0.6 to 1.2%, is used as the gelatinizer for magnesium as well as boron suspensions. The gelatinization of the suspensions is carried out by careful mixing, together with the gelatinizer, for several hours at an elevated temperature of 30-40°.

The magnesium suspensions thickened with aluminum octoate, stratify and change in viscosity during storage.

This is how the preparation and stabilization of suspensions containing 50% boron or magnesium is carried out, and this applies equally to the jet fuels JP-4 or JP-5 with stabilizers.

8. Utilization of Fuel Suspensions in Air-Reaction Engines

In connection with the ever-increasing requirements calling for

ever higher characteristics in fuels for air-reaction engines insofar as this pertains to an increase in thrust, and the efficiency and stability of combustion, much theoretical and experimental work has been done on the ignition of suspensions in air-reaction engines.

Suspensions of metals in hydrocarbon combustibles (fuels) show advantages over conventional aviation kerosenes as a result of their higher heats of combustion and combustion stability.

The utilization of special fuels for air-reaction engines is expedient in the case of special engines intended for high-speed flights, the takeoff of heavy aircraft, or for the acceleration of air-reaction engines in the case of rockets within the limits of the atmosphere.

For example, for the acceleration of cosmic rockets within the limits of the atmosphere, powerful turbojet and ramjet engines are being developed.

The acceleration of a rocket weighing several hundred thousand tons is accomplished by means of a guide-rail track some 20-30 km long, and powerful turbojet engines are used to develop speeds of up to 400-600 m/sec, after which the ramjet engines, which function to altitudes of 15-20 km, are actuated; at these altitudes, the rocket engines take over.

Elements such as boron and beryllium are of interest for air-reaction engines because on burning they release a greater quantity of heat than kerosene (more than 10,000 kcal/kg).

Great flight range can be achieved with such fuels.

On the other hand, interest is also expressed in elements which, although liberating a smaller quantity of heat on combustion than kerosene, liberate more heat per 1 kg of air than is required for the combustion process. In a VRD [ramjet] air is the working fluid.

Greater engine thrust can be obtained through the combustion of

TABLE 69

Heat of Combustion of Certain Fuels

1 Топливо	2 Формула	3 Теплота горения		
		4 ккал/кг	5 ккал/л	6 ккал/кг воздуха
7 Керосин	C_nH_m	10 300	8 200	720
8 Алюминий	Al	7 450	20 700	1 040
9 Бериллий	Be	16 210	30 400	2 130
10 Бор	B	14 100	33 400	1 480
11 Литий	Li	1 030	5 560	2 070
12 Магний	Mg	5 050	10 420	2 000
13 Пентаборан	B_5H_9	16 300	10 300	1 250

1) Fuel; 2) formula; 3) heat of combustion;
4) kcal/kg; 5) kcal/liter; 6) kcal/kg of air;
7) kerosene; 8) aluminum; 9) beryllium; 10)
boron; 11) lithium; 12) magnesium; 13) penta-
borane.

Fig. 62. Takeoff characteristics of a turbojet bomber
over a 3-meter obstacle. 1) 60%-magnesium suspen-
sion in the afterburner + injection of water; 2)
60%-magnesium suspension in afterburner; 3) conven-
tional fuel in afterburner; 4) no increase in
thrust due to augmentation in afterburner; A) take-
off distance, m.

such fuels, and such fuels are also suitable for acceleration of VRD.

For example, for the combustion of 1 kg of kerosene, 16 kg of air
are required; for the combustion of 1 kg of magnesium, only 2.2 kg of
air are required.

In addition to the above, the heat of combustion per unit fuel
volume is also important when the tank capacity of the engine is sig-
nificant.

Table 69 presents the heats of combustion for several fuels.

In connection with the above, ramjet engines using magnesium can develop a thrust greater by a factor of four than engines using kerosene, given equal engine cross sections.

Figure 62 presents figures demonstrating how the takeoff distance can be shortened for turbojet aircraft using magnesium suspensions.

When the JP-4 fuel is used in an engine and for thrust augmentation (afterburning), a bomber can take off in 4050 m, whereas with a 60%-magnesium suspension, the takeoff distance is reduced to 2400 m.

Figure 63 presents the relative value of missile flight range for ramjet engines operating on conventional JP-4 fuel, magnesium suspensions, as well as suspensions of boron and pentaborane.

In connection with the above, it is clear why such interest has been expressed in the utilization of metal suspensions for VRD.
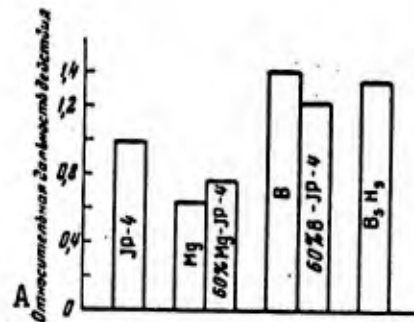
Fig. 63. Relative flight ranges for missiles with ramjet engines. Initial altitude, 18 km; the M(ach) number is equal to 3.2; trajectory in accordance with the Breguet formula [2]. A) Relative effective range.

In order to clarify the possibilities of using suspensions in VRD, a tremendous experimental project was undertaken to study the combustion of suspensions in special experimental installations, model ramjet engines, afterburners and, finally, in actual engines on a test stand and through flight tests of experimental aircraft [52].

Fig. 64. Theoretical character-
istics for the combustion of a
magnesium suspension. The num-
erals on the curves indicate
the content of Mg in octene-1,
in %, by weight. A) Temperature
of combustion, °K; B) excess-
combustible ratio; C) specific
air impulse, kg·sec/kg of air;
D) excess-air ratio.

Below we present calculation characteristics of theoretically pos-
sible fuel preparations for ramjet engines at pressures of 2 atm and
an air temperature at the inlet of 310°K.

Figure 64 presents the temperature of combustion and the specific
air impulse for a hydrocarbon combustible (octene-1 and magnesium) as
well as for suspensions of various compositions with magnesium, as
functions of the excess-combustible ratio.

With an increase in the magnesium compound in the suspension, the
temperature of combustion and the specific air impulse increase.

The specific air impulse as a function of the coefficient of ex-
cess combustible for the case of aluminum and boron and their suspen-

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sions is presented in Figs. 65 and 66.

The fuel-volume specific impulse obtained in the combustion of 1 kg of fuel has been plotted along the axis of ordinates, and the specific impulse per 1 kg of the air participating in the combustion and passing through the engine has been plotted along the axis of abscissas.

Figure 67 shows the effect that pressure and the excess-combustible ratio have on the specific air impulse in the combustion of a 50%-magnesium suspension.

In addition to the theoretical calculations, many experimental investigations were carried out on the combustion of suspensions in special test stands.

After the preliminary tests, the suspensions were ignited in a ramjet air-reaction engine having a diameter of 400 mm (Fig. 68).

The completeness of the combustion of the magnesium suspension exceeded 90% over a wide range of excess-air ratios. With an excess-combustible ratio of 0.7, the combustion of the magnesium was almost complete, although the efficiency of combustion for the hydrocarbon medium begins to drop at this point. These results can be seen in Fig. 69.

The completeness of the combustion of the boron suspension as a function of the excess-combustible ratio was studied in a small chamber, 47 mm in diameter and 200 mm long, as well as in a chamber 1300 mm long, under a pressure of 2.8 atm.

The data obtained with the small chamber, with a 30% suspension of boron in JP-4 fuel (with boron purities of 86 and 97%) are presented in Fig. 70.

The average particle dimension for the boron of 97% purity was 0.7 mμ. The completeness of boron combustion in a single specimen of the suspension (boron purity of 97%) amounted to 95%, whereas the com-
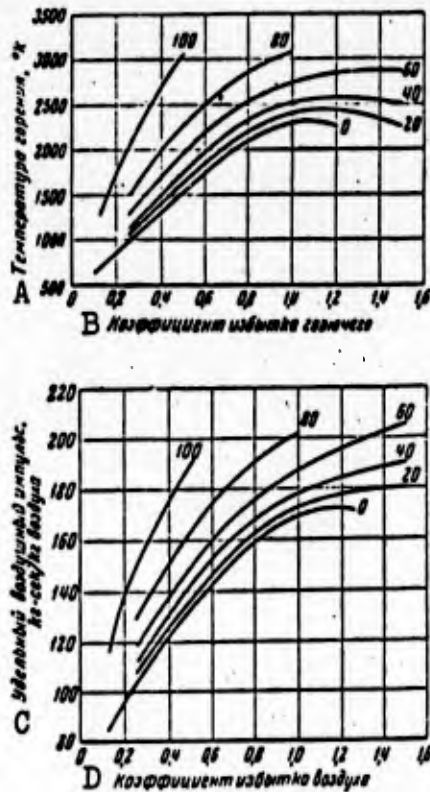
Fig. 65. Theoretical character-
istics of the combustion of an
aluminum suspension. The fig-
ures on the curves indicate
the Al content in the octene-1,
in % by weight. 1) Temperature
of combustion, °K; 2) excess
combustion [sic — probably com-
bustible] ratio; 3) specific
air impulse, kg·sec/kg of air;
4) excess-combustible ratio.

pleteness of combustion was only 80% in the case of the 86%-pure boron.

In the larger chamber of the ramjet engine, the efficiency of com-
bustion for 50% suspensions of boron did not exceed 80%. In this case,
a boron powder of 87-91% purity was used, and here the average par-
ticle dimension was 1 μ.

Successful flight tests of an aircraft with a ramjet engine were
carried out on a fuel consisting of a 50% suspension of magnesium. The
suspension consisted of 50% 0.6 and 1.5-micron magnesium in JP-4 avia-
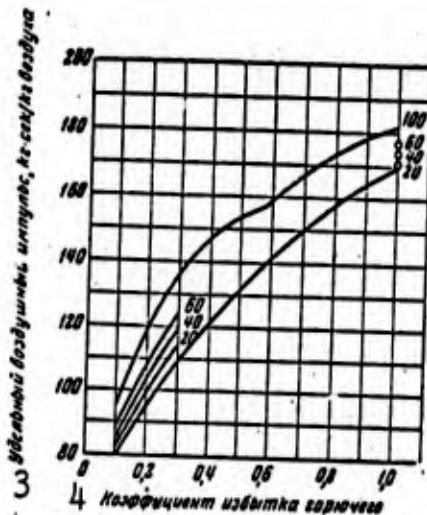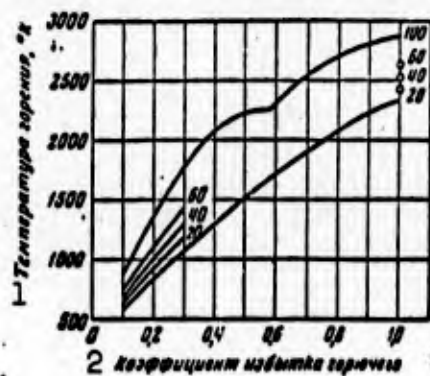
Fig. 66. Theoretical character-
istics for the combustion of
boron and its suspensions. The
figures on the curves indicate
the content of boron in the
octene-1 in % by weight. 1)
Temperature of combustion, °K;
2) excess-combustible ratio;
3) specific air impulse,
kg·sec/kg of air; 4) excess-
combustible ratio.

tion kerosene with an apparent viscosity of 7000 and 8000 centipoises.
The flights of the experimental aircraft with the ramjet engine, as-
sisted by means of rockets, proceeded successfully.

Magnesium suspensions burned efficiently, but could develop
greater thrust only in comparison with conventional hydrocarbons and
fuels, but could not offer any greater flight range.

Boron suspensions, without any special additives, did not burn
sufficiently completely and cannot be recommended for ramjet engines.
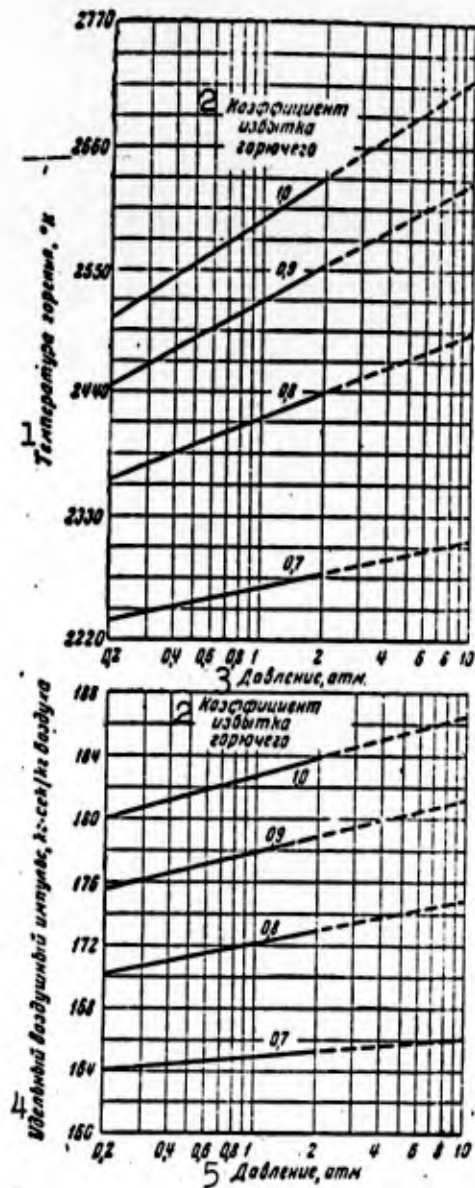
Fig. 67. Combustion character-
istics for 50% magnesium sus-
pensions at various pressures.
1) Temperature of combustion,
$^{\circ}$K; 2) excess-combustible ra-
tio; 3) pressure, atm; 4) spe-
cific-air impulse, kg·sec/kg
of air; 5) pressure, atm.

For the pumping of suspensions from the tanks to the combustion
chamber of the engine, special centrifugal pumps were designed.

Air vaporization was employed in the injectors, in view of the
high viscosity of the suspensions.

The combustion stability of 50% magnesium suspensions was very
much greater than in the case of conventional fuels. For example, given
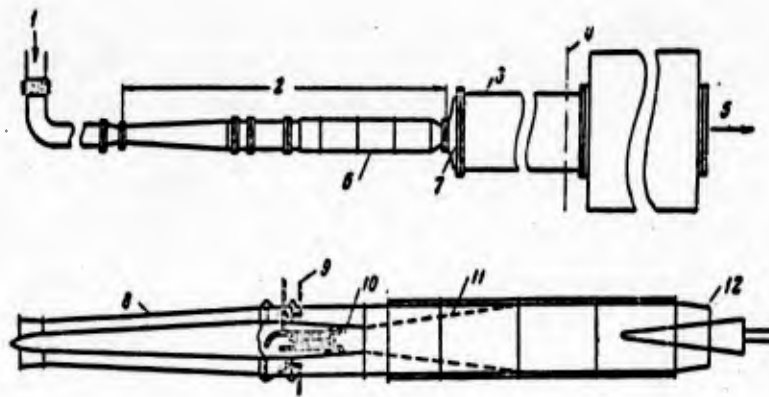
Fig. 68. Ramjet engine, diameter 400 mm, used for
the investigation of the combustion of boron fuels
[2]. 1) Air; 2) 400-millimeter ramjet engine; 3)
calorimeter; 4) thermocouple; 5) high-altitude ex-
haust; 6) combustion chamber; 7) water jet; 8) dif-
fuser; 9) fuel; 10) igniter; 11) flame holder; 12)
variable-area nozzle.
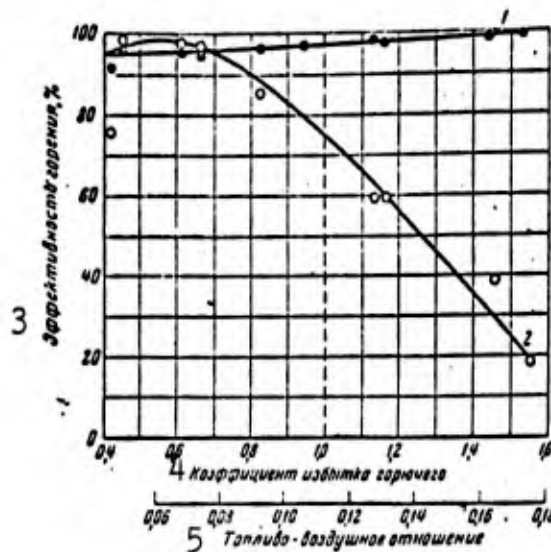
Fig. 69. Effect of the excess-combus-
tible ratio and the fuel-to-air ra-
tio on the efficiency of the combus-
tion of a suspension containing 50%
24-micron magnesium in JP-3 fuel with
0.8% gelatinizing additive (1), and
JP-3 fuel (2); 3) combustion effi-
ciency, %; 4) excess-combustible ra-
tio; 5) fuel-to-air ratio.

equal excess-combustible ratios, flame detachment in the case of JP-4

aviation kerosene takes place in an experimental engine at a velocity

of 20 m/sec for the air stream, and in the case of the 50% magnesium

suspension, the flame detachment takes place at 30-32 m/sec.
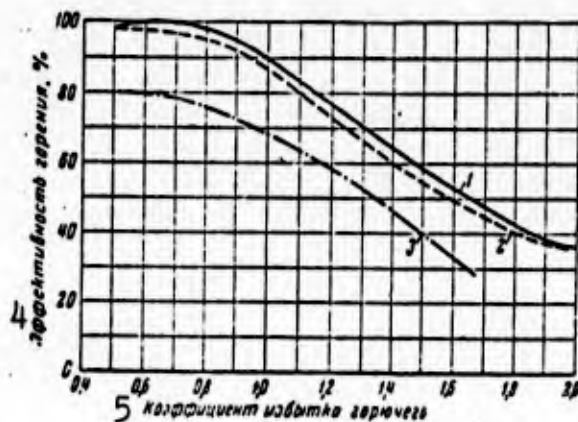
Fig. 70. Combustion efficiency (com-
pleteness of combustion) of JP-4 fuel
and two 30% boron suspensions pre-
pared with JP-4 fuel. 1) JP-1; 2)
97%-pure boron; 3) 86%-pure boron;
4) combustion efficiency, %; 5) ex-
cess-combustible ratio.

Thus basically magnesium suspensions are proposed for acceleration
systems for aircraft and possibly rockets, given the continued improve-
ment of the feed systems; the problem of using boron suspensions was
not resolved in the cited investigations in view of the inadequate
completeness of combustion.

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[Footnotes]

198 The cost of 1 kg of metallic beryllium in the USA is $130.

210 At the same time, it was reported that the cost of 1 kg of
    of pentaborate [sic.] in the USA in 1958 was $800.

[List of Transliterated Symbols]

222 $l_g = \log$

Chapter 6

COMPLETENESS OF FUEL COMBUSTION AND CARBON
FORMATION IN AIR-BREATHING JET ENGINES

1. COMPLETENESS OF JET-FUEL COMBUSTION

The entire quantity of heat that corresponds to the fuel's heating value is not liberated when fuel is burned in an engine. The reason for this consists in the formation of a certain quantity of carbon monoxide, deposition of carbon in the form of an elementary deposit, and the formation of a small quantity of pyrolysis products of the fuel (hydrocarbon gases).

The ratio of the quantity of heat actually liberated on combustion of a unit weight of fuel, Q_f, to the lower-limit heating value Q_n reflects the degree to which the heat is utilized in the engine. This ratio is known as the heat-evolution factor or the combustion efficiency. The heat-evolution factor $\eta_z = Q_f/Q_n$. The ratio Q_f/Q_n expressed in percent is usually known as the completeness of combustion (φ).

$$\varphi = \frac{Q_\phi}{Q_{_H}} \cdot 100.$$

Under the engine's normal operating conditions, the completeness of combustion reaches 94-98%, but under unfavorable conditions (see below) it may drop to 75-80%, which is equivalent to a 20-25% heat loss.

The combustion process of the fuel in an air-breathing jet engine takes place in the primary combustion-chamber zone at a tempera-

ture of 1900-2200° with a quantity of air close to the quantity theoretically necessary. Then the products of combustion are diluted by an excess of air, with the result that the temperature of the gases has dropped to 750-850° (secondary zone) before arrival at the turbine. The necessity of lowering the gas temperature is associated with the limited high-temperature corrosion resistance of the turbine blades. The additional air also cools the components of the engine. As a result, the gases flowing from the nozzle of an air-breathing jet engine contain a considerable excess of oxygen in addition to CO_2, H_2O, and N_2.

Some incompleteness of combustion is noted in practice even with an excess of air present.

The ratio of the quantity of air supplied to the engine to the quantity theoretically necessary for combustion of fuel is known as the excess-air ratio.

The completeness of combustion and the excess-air ratio may be determined from gas analysis of the combustion products, and if the excess-air ratio is known, the completeness of combustion is determined from the other parameters that characterize the evolution of heat, e.g., the combustion temperature. In turbojet engines, the excess-air ratio is considerably greater than unity and comes to $\alpha = 4$ to 6 in the basic operating modes.

Let us consider as an example combustion of cyclohexane with an inadequate quantity of air ($\alpha = 0.835$), with the theoretically necessary quantity of air ($\alpha = 1$) and with an excess of air ($\alpha = 4$):

$$C_6H_{12} + 7\tfrac{1}{2}O_2 + 28,2N_2 \rightarrow 3CO_2 + 3CO + 6H_2O + 28,2N_2 \qquad (1)$$
$$C_6H_{12} + 9O_2 + 34N_2 \rightarrow 6CO_2 + 6H_2O + 34N_2 \qquad (2)$$
$$C_6H_{12} + 36O_2 + 135N_2 \rightarrow 6CO_2 + 6H_2O + 27O_2 + 135N_2 \qquad (3)$$
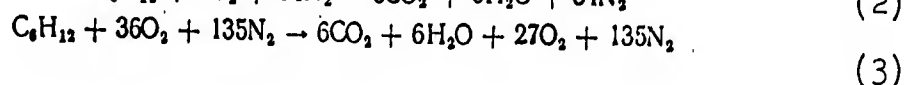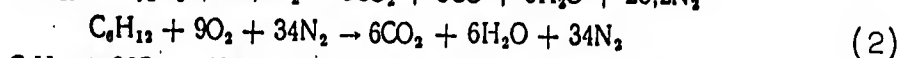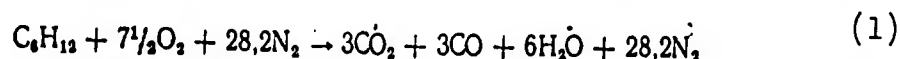
Equations (1)-(3) have been written on the basis of the air composition $O_2 + 3.76\ N_2$.

As we have already noted, certain fuel losses (2-5%) take place as a result of incomplete combustion even with an excess of air. This can be accounted for by the fact that the combustion process is completed in a short time (in approximately $1 \cdot 10^{-3}$ sec), and the fuel does not have time to burn completely.

Applying Eqs. (2) and (1), let us find the completeness of combustion of cyclohexane from the composition of the combustion products.

For this purpose, we must divide the quantity of heat evolved in incomplete combustion of cyclohexane by the quantity of heat that would be evolved in complete combustion:

$$\varphi = \frac{CO\% \cdot 26.84 + CO_2\% \cdot 94.45 + H_2O\% \cdot 57.84}{CO_2\% \cdot 94.45 + H_2O\% \cdot 57.84} \cdot 100,$$

where CO, CO_2, and H_2O represent the composition of the combustion products in moles (on the basis of the combustion equation) or percentages by volume found by gas analysis. In experimental determination of combustion completeless on the basis of gas composition, the sum $CO + CO_2$ in the combustion products corresponds to the quantity of CO_2 corresponding to complete combustion. The quantity of water vapor is not determined experimentally, but computed from the chemical formula or elementary composition of the fuel.

According to Eq. (3), the completeness of combustion of cyclohexane is 77.8%; this corresponds to a heat-evolution factor of 0.778 or to the evolution of 8100 kcal/kg in incomplete combustion.

In air-breathing jet engines, the completeness of combustion depends on the chemical and fractional composition of the fuel. Here it is necessary to remember that when the combustion process is "well-organized," combustion may go to 95-98% of completion, and in this case the influence of fuel composition will be unnoticeable, since all of the fuel will burn with evolution of the same quantity of heat.

However, the conditions under which fuels are used in engines are variable and not restricted to the basic mode. Combustion of the fuel in the engine may take place under complicated conditions in which the completeness of combustion amounts to 75-85%. Combustion at depressed pressures (below 0.8-1 atmosphere), combustion with large excesses of air cooling the combustion zone, combustion at low engine rpm's, etc., constitute complicated conditions.

Under these conditions, completeness of combustion comes to depend on the chemical and fractional composition of the fuel. At first glance, it may appear that fuel composition exerts no influence, since the basic combustion process takes place at high speeds and temperatures from 1900 to 2200°, i.e., under conditions under which the oxidation rate is so large that fuel composition cannot affect it.

However, more detailed examination of the combustion process leads us to the contrary conclusion.

The fuel-combustion process is a complex and multi-stage set of physical and chemical phenomena that unfold at various temperatures. The physical phenomena include atomization of the fuel, its vaporization, the formation of a vapor-and-air mixture and heating of the combustible mixture. The chemical phenomena include the oxidation reactions of the fuel in the preignition zone, with the result that intermediate combustion products — various oxygen-containing compounds — are formed.

The next stage is that of self-ignition or firing of the combustible fuel-air mixture by the heated products of combustion. It includes a sharp increase in the rates of the chemical reactions to values characteristic for the formation of the ultimate combustion products. The more complex the fuel composition, the more probable

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are preignition processes and the more important will be the part that they take in combustion. Thus, for example, in combustion of pentane, the reactions of cracking and low-temperature oxidation are less probable in the preignition zone than in the combustion of, for example, hexadecane.

At moderate temperatures from 100 to 300°, hexadecane undergoes considerable oxidation at a higher rate than does pentane, and is also much more easily cracked. If combustion develops in advance of the flame front through self-ignition of microvolumes of fuel with air, it will go farther toward completion with paraffinic hydrocarbons than with aromatic hydrocarbons, since paraffinic hydrocarbons have lower self-ignition points. However, the role taken by the preignition processes and intermediate products in combustion of hydrocarbon fuels in air-breathing jet engines is unknown. It would appear that the importance of the chemical composition of the fuel and various minor additives reduces to stimulation of the preignition processes, i.e., stimulation of reactions in a relatively low-temperature region (below the combustion temperature). It may be found that as a result of poor mixing or low pressure, such processes in the preignition zone as the oxidation, self-ignition, and ignition reactions of the vapor-air combustible mixture will be protracted and, consequently, this will be the slowest stage, and one that retards the process as a whole. In this case, combustion of the fuel will depend to a considerable degree on the chemical composition of the fuel (since reactions in the preignition zone, which depend on fuel and additive composition) will acquire greater significance, and the influence of additives that stimulate the initial stages of combustion will also be noticeable.

It would also be of interest to take completeness of combustion

into account in the light of the fact that the specific fuel consumption rises when it is not completely burned and, consequently, the flight range of the aircraft is shortened. The specific fuel consumption for an air-breathing jet engine may be characterized by the following equation as a function of heating value and completeness of combustion (See Chapter 1):

$$C_{y\text{д}} = \frac{3600 \cdot g_{\text{т}}}{\frac{1}{g}\left\{\sqrt{2g\,427\eta_e\eta_i \cdot \frac{Q \cdot \eta_s}{\alpha L_0} + v^2} - v\right\}},$$

where Q is the heating value, g_t is the ratio of fuel to air weight, η_z is the heat-evolution factor, $\underline{v}$ is the flight speed and $\underline{g}$ is the acceleration of gravity.

Accordingly, the specific consumption of a fuel with a heating value of 10,250 kcal/kg and the flight range vary as functions of the completeness of combustion, as follows:

1) Полнота сгорания	2) Удельный расход топлива, кг в час на кг тяги	3) Снижение дальности полета, %	1) Полнота сгорания	2) Удельный расход топлива, кг в час на кг тяги	3) Снижение дальности полета, %
1,00	1,0	—	0,85	1,18	18
0,95	1,05	5	0,80	1,20	20
0,90	1,11	11	0,75	1,33	33

1) Completeness of combustion; 2) specific fuel consumption, kg per hour per kg of thrust; 3) loss in range of flight, %.

Apart from the design features of the engine, completeness of combustion depends on the pressure at which the process occurs. Combustion completeness drops considerably at pressures below 1 atmosphere.

The pressure at which combustion of fuel occurs depends on the degree to which the air is compressed by the turbojet's compressor, on altitude, and on flight speed.

At a flight speed of 750-800 km/hr, the combustion-chamber pressure is determined by the pressure of the surrounding atmosphere and the compression of the air by the compressor (Table 70).

TABLE 70

Air Pressure and Pressure in Chamber of Turbojet Engine at Different
Altitudes (without taking velocity head into consideration)

1) Высота над уров- нем моря, м	2) Давление воздуха		5) Давление (атм) в камере двигателя при степени сжатия		
	3) мм рт. ст.	4) атм	4	6	10
3 000	520	0,690	2,75	4,10	6,90
5 000	405	0,530	2,10	3,20	5,30
10 000	198	0,260	1,04	1,50	2,60
11 000	169	0,222	0,89	1,32	2,22
12 000	145	0,191	0,76	1,14	1,91
13 000	124	0,162	0,65	0,97	1,62
15 000	91	0,120	0,48	0,72	1,20
16 000	77	0,110	0,44	0,66	1,10
20 000	41	0,0540	0,21	0,320	0,54

1) Altitude above sea level, m; 2) air pressure; 3) mm Hg; 4) atmos-
pheres; 5) pressure (atmospheres) in engine chamber at compression
ratio of.

At flight speeds above 1000 km/hr, the air is precompressed by

the velocity head.

In this case, the pressure value may be determined by the formula

$$p = p_0 (1 + 0.2 M^2)^{\frac{k}{k-1}},$$

where M is the Mach number (which is equal to unity at the speed of

TABLE 71

Pressure of Decelerated Air Flow in Ramjet Engine as a Function of
Flight Altitude and Speed

1) Высота над уровнем моря, км	2) Давление (атм) заторможенного потока воздуха при числе M *.				
	M = 0	M = 1	M = 1,5	M = 2	M = 3
10	0,270	0,51	0,99	2,10	9,90
15	0,120	0,23	0,43	0,96	4,50
20	0,054	0,11	0,20	0,22	2,05
25	0,030	0,05	0,09	0,20	0,93

*M is the Mach number. This number is used to characterize speed.
At M = 1, the speed thus characterized is equal to that of sound
(~ 1200 km/hr).

1) Altitude above sea level, km; 2) pressure (atmospheres) of de-
celerated air flow at Mach* number of.

sound, 330 m/sec), k/(k — 1) is 3.5 for air. At flight speeds of 1 to

2 times the speed of sound, we observe considerable precompression of

the air; this is known as decelerated-flow pressure (Table 71).

TABLE 72

Completeness of Combustion for Various Fuels in
Stationary Testing Under Conditions Equivalent to
Flight Conditions [1]

1) Топливо	2) Пределы выкипания, °C	3) Полнота горения, %	4) Выделение тепла, ккал/кг
5) Авиационный бензин	53—174	85	8900
6) Топливо широкого фракционного состава	60—240	83,5	8700
7) Авиационный керосин	148—264	·83	8500

1) Fuel; 2) boiling range, $^\circ$C; 3) completeness of
combustion, %; 4) heat evolved, kcal/kg; 5) avia-
tion gasolines; 6) broad-fraction fuel; 7) aviation
kerosene.

TABLE 73

Completeness of Fuel Combustion at High
Altitude as a Function of Ratio of Air
to Fuel and Chemical Composition of Fuel
[1, 2]

1) Топливо	2) Групповой состав, %	3) Полнота горения (%) при отношении воздух : топливо	
		40	80
4) Авиационный керосин . . 5) Ароматические — 19,4 6) Нафтены — 39,2 7) Парафины — 41,4		84	81,5
8) Концентрат парафиновых 9) углеводородов 10) н. к. 159° к. к. 265°		·83,5	84
11) Концентрат ароматических углеводородов 12) н. к. 166° 13) к. к. 253°	5) Ароматические — 75,2 6) Нафтены — 11,4 7) Парафины — 13,4	82,5	77

1) Fuel; 2) group composition, %; 3) complete-
ness of combustion (%) at air:fuel ratio of;
4) aviation kerosene; 5) aromatic; 6) naphthenes;
7) paraffines; 8) paraffinic-hydrocarbon con-
centrate; 9) initial boiling 159°; 10) end of
boiling 265°; 11) aromatic-hydrocarbon concen-
trate; 12) initial boiling 166°; 13) end of
boiling 253°.

The heat loss due to incomplete combustion depends on where com-

bustion takes place — in the turbojet-engine chamber or in the afterburner — and on the degree to which the air is compressed in the engine.

In ramjet engines, compression of the air is effected only by the velocity head, so that at flight speeds of the order of 2400-3600 km/hr at a 25-km altitude, the pressure in the engine will be lower than 1 atmosphere.

When an additional quantity of fuel is burned in the afterburners of a turbojet engine at flight speeds of 1200-1800 km/hr, the combustion process at altitudes of 12 to 20 km apparently always takes place at depressed pressures, and considerable incompleteness of combustion may be expected in these cases.

Let us examine experimental data on the completeness of combustion for various fuels.

The completeness of fuel combustion is shown in Table 72 as a function of fractional composition.

As noted above, completeness of combustion depends on the quantity of air passing through the engine.

Table 73 shows the completeness of fuel combustion at high altitude as a function of the chemical nature of the fuel and the excess-air ratio.

Under favorable conditions, the difference in combustion completeness between paraffinic and aromatic hydrocarbons virtually vanishes (air:fuel ratio 40, $\alpha = 2.5$).

With large air excesses (air:fuel ratio 80 to 100), at which considerable cooling of the combustion zone apparently takes place, we observe a drop in completeness of combustion, particularly with aromatic hydrocarbons [3, 4].

Figures 71 and 72 show the influence of chemical composition and

engine operating mode (air:fuel ratio) on the completeness of fuel combustion at a combustion-chamber pressure of 1.3 atmospheres. At an air:fuel ratio of 60 ($\alpha \simeq 4$), all fuels burn to about 98% of completion. However, under less favorable conditions ($\alpha \sim 8$), the completeness of fuel combustion drops off, and does so most sharply in the aromatic hydrocarbons.

Figure 73 shows the effectiveness of combustion as a function of fuel fractional composition for various engine operating modes. As we have already noted, completeness of combustion shows virtually no dependence on fuel fractional composition under favorable conditions, but with large air excesses ($\alpha = 4$ to 8), differences appear in the combustion efficiency, which is highest for the light fuels.

The heat-evolution factor in combustion of various fuels under high-altitude conditions is shown in Fig. 74 [5] as a function of fuel chemical composition. In plotting the diagram, the efficiency of heat evolution for standard fuel was taken as 100.

We observe the greatest amount of evolved heat per unit weight on combustion of fuels under high-altitude conditions in the paraffinic hydrocarbons, and the highest figure per unit volume in the aromatic hydrocarbons, although these are distinguished by lower completeness of combustion.

Normally, the fuel is fed into the combustion chamber in liquid form, where it is atomized by centrifugal nozzles, mixed with air, and ignited. Combustion chambers for burning prevaporized fuel have recently been developed.* In vaporizing-type chambers, completeness of combustion is also a function of fuel chemical composition [6].

The variation of fuel-combustion efficiency for fuels of various chemical compositions is shown in Fig. 75 as a function of air:fuel ratio in the chamber with vaporization of the fuel.

In 1954, a paper by Sharp [6] devoted detailed consideration to the influence of the chemical and fractional composition of the fuel on the combustion-chamber characteristics as regards completeness of combustion and carbon formation, and to the limits within which it is possible to reduce the influence of fuel type by improving the combustion chamber.

The characteristics of fuels F and E, which were used in the investigations, are presented in Table 74.

TABLE 74

Characterization of Tested Fuels E and F

	1) Фракционный состав, °C					4) Плотность	5) Вязкость, сст	6) Содержа-ние аро-матиче-ских,%
2) н. к.	10%	50%	90%	3) к. к.			
7) Топливо E	188	206°	222°	264°	309°	0,87	2,2	23
8) Топливо F	87	172°	163°	215°	236°	0,78	0,87	10

1) Fractional composition, °C; 2) initial boiling; 3) end of boiling; 4) density; 5) viscosity, centistokes; 6) aromatic-hydrocarbon content, %; 7) fuel E; 8) fuel F.
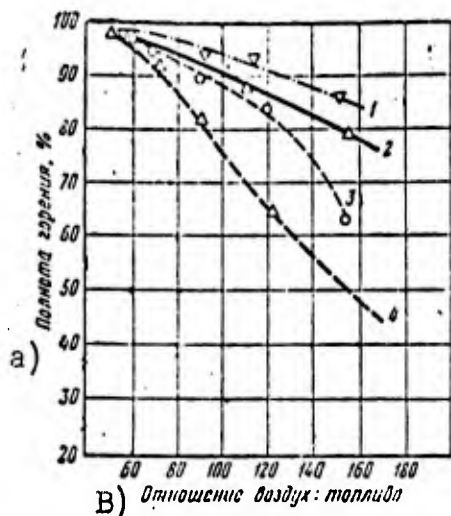
Fig. 71. Influence of chemical composition of fuel and operating mode of engine (air:fuel ratio) on completeness of combustion; 1) Technical isooctane, b.p. 72-94°; 2) technical isooctane with b.p. 96-109°; 3) isodecane with b.p. 164-198°; 4) aviation kerosene with b.p. 151-273°. A) Completeness of combustion, %; B) air:fuel ratio.
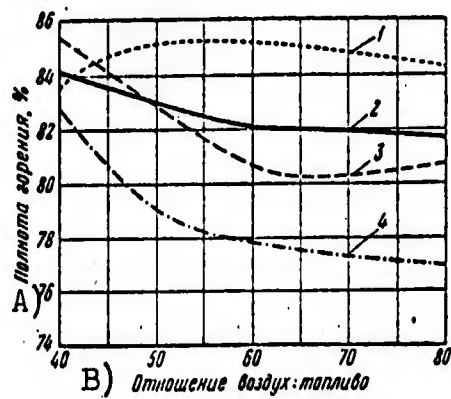
Fig. 72. Influence of chemical composition of fuel and engine operating mode on completeness of combustion. 1) Paraffinic; 2) standard; 3) naphthenic; 4) aromatic. A) Completeness of combustion, %; B) air:fuel ratio.
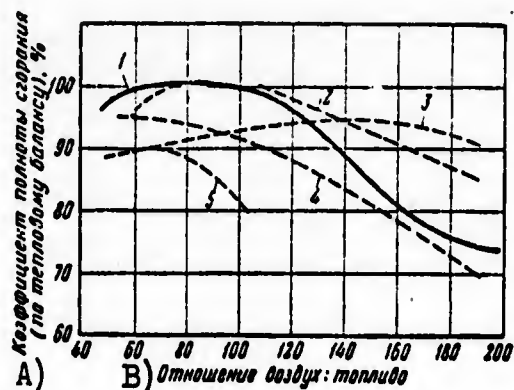
Fig. 73. Efficiency of fuel combustion as a
function of fractional composition at in-
coming-air pressure of 0.57 atmosphere and
temperature of 125°. 1) Broad-fraction fuel;
2) mixture of 50% gasoil and 50% gasoline;
3) gasoline; 4) aviation kerosene; 5) gasoil.
A) Combustion completeness factor (from ther-
mal balance), %; B) air:fuel ratio.
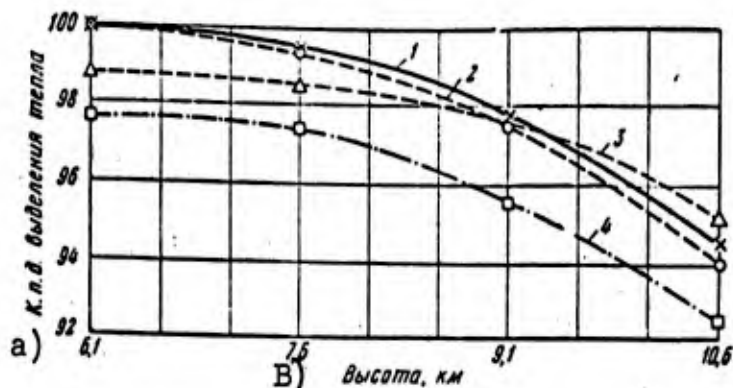
Fig. 74. Heat-evolution factor in combustion
of various fuels under high-altitude conditions.
1) Standard RT-2978; 2) naphthenic; 3) paraffinic;
4) aromatic. A) Efficiency of heat evolution;
B) altitude, km.
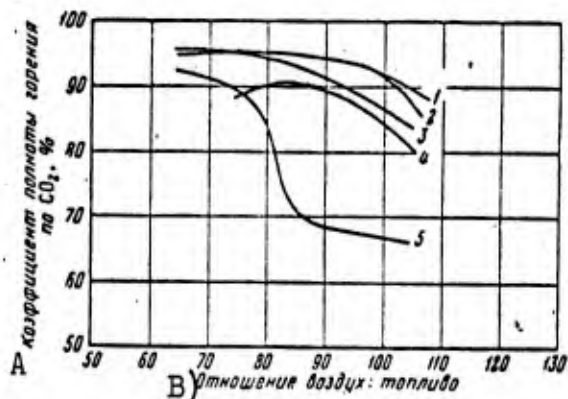
Fig. 75. Influence of chemical nature of fuel and
air:fuel ratio on completeness of combustion in
vaporizer-type chamber at air pressure of 0.63 atmos-
phere and temperature of 60°. 1) Cyclohexane;
2) isopropylbenzene; 3) benzene; 4) xylene; 5) toluene.
A) Combustion completeness factor based on CO_2, %;
B) air:fuel ratio.
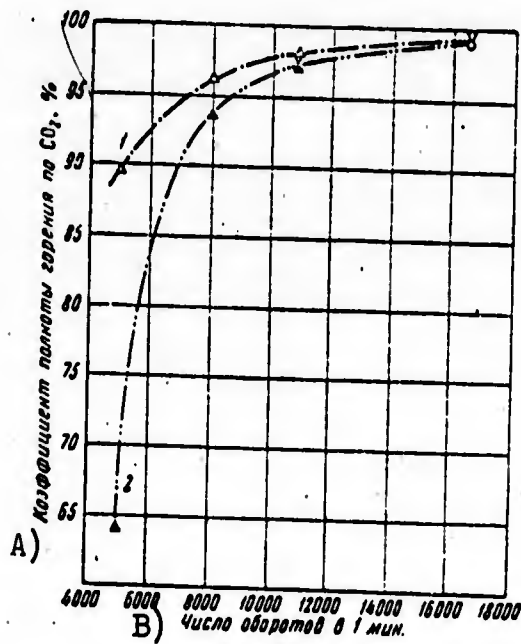
Fig. 76. Combustion-completeness ratio of fuel as a function of engine rpm's at sea level. 1) Fuel F; 2) fuel E. A) Combustion-completeness ratio based on CO_2, %; B) rpm.
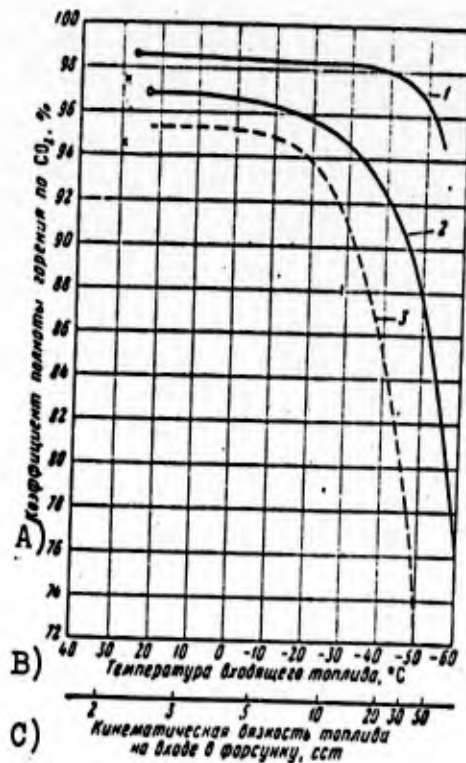
Fig. 77. Influence of fuel viscosity (standard gasoil) and nozzle type on combustion-completeness factor at pressure of 0.8 atmosphere and air temperature of 125°. 1, 2, 3) Various types of nozzles; A) Combustion-completeness ratio based on CO_2, %; B) entry temperature of fuel, °C; C) kinematic viscosity of fuel at entry into nozzle, centistokes.
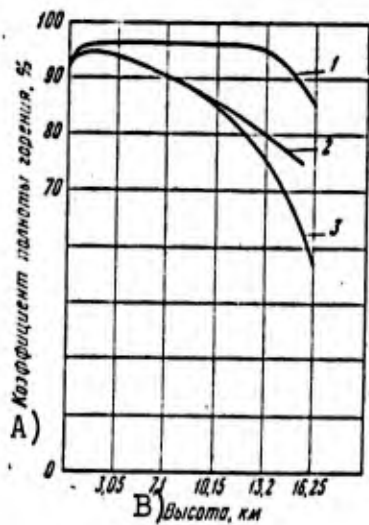
Fig. 78. Change in combustion-completeness factor in engine and nozzle chamber at various altitudes. 1) Engine; 2) chamber, 25% augmentation; 3) chamber, 17% augmentation; A) Combustion-completeness ratio, %; B) altitude, kilometers.

The influence of the chemical composition and volatility of the fuel is manifested chiefly in unfavorable engine operating modes. This is illustrated by Fig. 76, which shows completeness of fuel combustion (characterized by ratio of CO_2 in combustion products to theoretical quantity of CO_2) as a function of engine rpm's between 4000 and 16,000. At normal rpm's (10,000-16,000), the fuels were equivalent in completeness of combustion. At low rpm's, i.e.,

with reduced air and fuel flow rates and pressures, fuels having high volatility and low aeromatic-hydrocarbon content give considerably higher completeness of combustion. Thus, fuel E (density 0.87), which contained 23% of aromatic hydrocarbons, burned to 85% of completion with the engine turning at 6000 rpm, while fuel F (density 0.78), which contained 10.6% of aromatic hydrocarbons, burned to 92.5% of completion.

The relationship between completeness of fuel combustion and chemical composition is manifested with particular distinctness as the air excess is increased, but these differences can be reduced by improving atomization.

The viscosity of the fuel influences its atomization and the quality of mixture formation, which, in turn, are reflected in the completeness of combustion. However, this effect depends on the elegance with which the process of atomization and mixing the fuel with air is set up (Fig. 77).

Highly interesting data on combustion of fuels in afterburners [7] were published in 1955.

The afterburner is an elongated jet-engine nozzle in which a supplementary quantity of fuel is burned. This is made possible by virtue of the fact that the combustion products entering the jet nozzle after the turbine have a high temperature (500-600°) and a considerable oxygen excess, since the combustion process in the engine chamber proceeds at 4-6 α.

The beginning of development of afterburners to increase the thrust of turbojet engines dates from the period from 1949-1950.

Modern afterburners are used for the following purposes:

1) to assist takeoff of heavy bombers from the ground;

2) to increase the speed of interceptors.

The afterburner pressure depends on the altitude and speed of flight. At subsonic speeds and high altitudes, the pressure in the afterburner is low and the range of stable combustion is narrow.

An afterburner can be used to increase the thrust developed by the engine, but the specific fuel consumption rises considerably when this is done. This will be evident from the following data:

thrust developed by engine at surface, kg...............7,700

fuel consumption, liters per hour.......................9,350

specific fuel consumption, liters/hour·kg.............. 1.22

thrust with afterburner cut in, kg....................10,900

afterburner thrust, kg.................................3,200

fuel consumption with afterburner in operation,
    liters/hour......................................19,500

fuel consumption in afterburner, liters/hour...........10,195

specific fuel consumption, liters/hour·kg............. 3.18

At flight speeds below 1800 km/hr, the fuel consumption increases to 45,460 liters/hr with the afterburner operating.

Experimental data on the performance of engines with afterburners under high-altitude conditions are of great importance, but it is very difficult to secure them.

Normally, the tests are carried out in wind tunnels, on flying "laboratory" aircraft, or in ordinary aircraft.

Figure 78 shows the variation of the fuel-combustion completeness factor under flight conditions in an engine equipped with an afterburner.

At an altitude of 16 km the combustion-completeness factor in the afterburner is 75%.

At high altitudes, a major part of the thrust is produced in the afterburner, which functions as a ramjet engine, while the turbojet

engine is essentially an appendage to it [7].

Apart from investigation of fuel-combustion completeness under various conditions of application in full-sized engines and models, study of this problem on small laboratory instruments is of interest in the first stage of research.

The use of laboratory methods with the object of determining the characteristics of a fuel is advisable, since it enables us to work with small quantities of fuel and individual hydrocarbons that are not available for testing on large scales.

The author developed [8] a special laboratory apparatus with a ramjet-type combustion chamber (Fig. 79) for study of combustion completeness in individual hydrocarbons.

The chamber consists of a cylindrical section open at both ends. Air-atomized fuel is fed into the lower part, which is 70 mm in diameter and 200 mm long, at a rate of about 1 g/sec. The fuel, which has been mixed with air, is ignited by an electric spark (or by a special miniature burner) and burns. The combustion products issue from the top, nozzle part of the chamber, which is 30 mm in diameter. Ignition of the fuel sets up an intensive flow of air, in an excess of which ($\alpha = 1.38$) combustion of the fuel takes place. The completeness of combustion is determined from the composition of the gas tapped from the center section of the chamber through a special tube into a vacuum burette.

The completeness of fuel combustion is determined by gas analysis from the quantity of CO and CO_2 that has formed (it is assumed that the hydrogen of the fuel has burned to form water). Special gas analyzers that make it possible to determine CO and CO_2 in concentrations to hundredths of a percent are used for analysis of the combustion products, which are diluted with a large quantity of air.
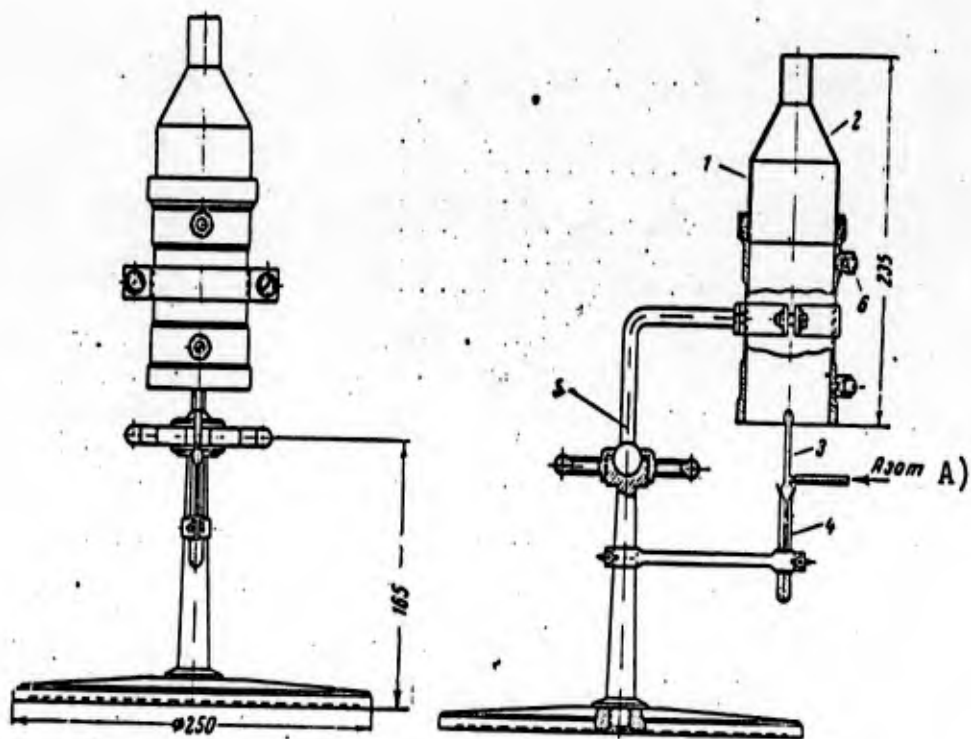
Fig. 79. Scheme of laboratory combustion chamber for study of relative completeness of combustion and carbon formation in individual hydrocarbons and fuels. 1) Cylindrical section of combustion chamber; 2) nozzle section of combustion chamber; 3) air nozzle; 4) container with fuel; 5) stand; 6) hole for tapping gas. A) Nitrogen.

The combustion completeness of the fuels was studied in both the atomized and vaporized forms.

When the fuel is burned in vaporized form, the influence of such physical factors as atomization and vaporization is excluded, and the part taken by the fuel's chemical structure is more apparent.

Table 75 lists combustion-completeness figures for individual hydrocarbons.

The completeness of combustion of vaporized fuels is somewhat higher than that of atomized fuels. Naturally, this difference is related to a certain combustion-chamber design, since with clean combustion — to 97-98% of completion — it is not observed. In principle, however, the vaporized-fuel combustion experiments indicate an influence of the fuel's chemical composition on the combustion process.

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Figure 80 shows the completeness of combustion of kerosene-type fuels as a function of aromatic-hydrocarbon content and the excess-air ratio (α = 1.38 and 3.4). With α = 3.4, combustion of the fuel was effected in an elongated combustion chamber without constriction of the nozzle section. The completeness of combustion decreases consistently as the quantity of aeromatic hydrocarbons is increased [8].

TABLE 75

Heat of Combustion of Individual Hydrocarbons in Atomized and Vaporized States in Laboratory Combustion Chamber [8]

1) Углеводород	Полнота горения, %, 2)	
	3) распыленное топливо	4) испаренное топливо
5) Гептан	80	82,5
6) Циклогексан	78	81,5
7) Циклогексен	76	79,3
8) Бензол	70	73,8
9) Изопропилбензол	72,5	74,3
10) Тетралин	71	74
11) Метилнафталин	66	68,3
12) Декалин	76	79,8

1) Hydrocarbon; 2) completeness of combustion, %;
3) atomized fuel; 4) vaporized fuel; 5) heptane;
6) cyclohexane; 7) cyclohexene; 8) benzene; 9) isopropylbenzene; 10) tetralin; 11) methylnaphthalene;
12) decalin.

Thus, the completeness of combustion increases in the following series of hydrocarbons as a function of chemical composition:

$$\text{aromatic bicyclic} < \text{aromatic monocyclic} < \text{aromatic monocyclic with side chains} <$$

$$< \text{naphthenic bicyclic} < \text{cycloolefins} < \text{monocyclic naphthenes} < \text{paraffins}$$

This applies for fuels that enter the combustion chamber in the atomized state or in the form of vapor.

It should be remembered, however, that completeness of combustion depends not only on the chemical, but also on the fractional composi-
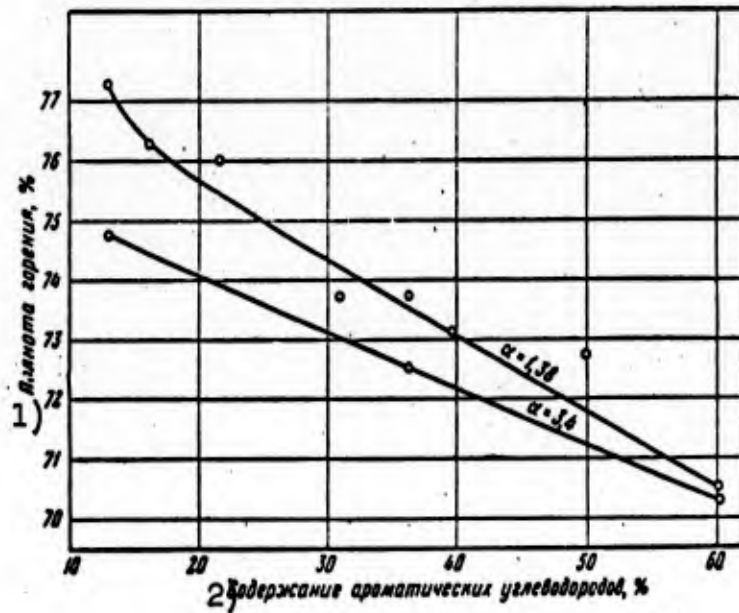
Fig. 80. Variation of combustion completeness
as a function of aromatic-hydrocarbon con-
tent in kerosene-type fuels for two excess-
air ratios. 1) Completeness of combustion,%;
2) aromatic-hydrocarbon content, %.

tion or on the boiling point of the individual hydrocarbons. Hence

a distinct influence of the hydrocarbons of various series is ob-

served only in fuels with closely similar fractional compositions.
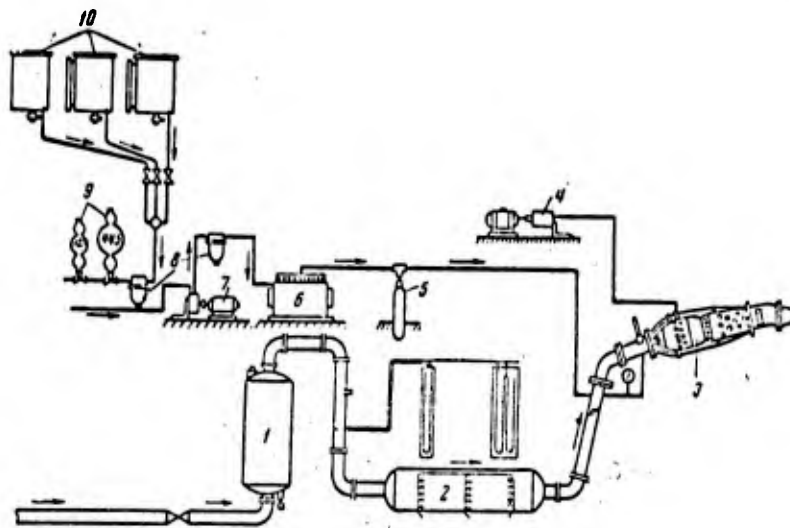
Fig. 81. Schematic diagram of miniature single-
chamber apparatus. 1) Receiver; 2) electric air
preheater; 3) miniature combustion chamber; 4)
starting magneto; 5) fuel receiver; 6) fuel pump;
7) fuel booster pump; 8) fuel filters; 9) spot
samplers; 10) fuel tanks.

In concluding our discussion of the combustion-completeness problem, however, we should note that the research material published on this topic is as yet inadequate to form a basis for judging the degree to which incomplete combustion will lower the efficiency of the engines under all conditions of application of the fuel.

However, there is no question that when the completeness of combustion diminishes, the specific fuel consumption increases and the flight range decreases.

Increasing the completeness of fuel combustion by manipulating various factors under high-altitude conditions (in cases where completeness is below 95-97%) makes it possible to increase flight range, since an increase in combustion completeness is essentially equivalent to an increase in heating value.

There are no sufficiently detailed data available on completeness of fuel combustion in turbojet and ramjet engines under various conditions of application. This question requires clarification in each specific case.

The completeness of aviation-fuel combustion has been studied in detail by Soviet investigators using stationary test apparatus. A schematic diagram of a scaled-down single-chamber apparatus for investigation of combustion completeness is shown in Fig. 81. The chamber of the apparatus simulates the fuel-combustion process as it takes place under real conditions [9].

The completeness of fuel combustion was evaluated by recording curves of the heat-evolution factor as a function of combustible-mixture composition with an air flow rate of 0.25 kg/sec at an air temperature of 60°.

The heat-evolution factor is computed by the formula

$$\eta_z = \frac{C_p t_z (G_b + G_m) - C_p t G_b}{G_m - H_u},$$

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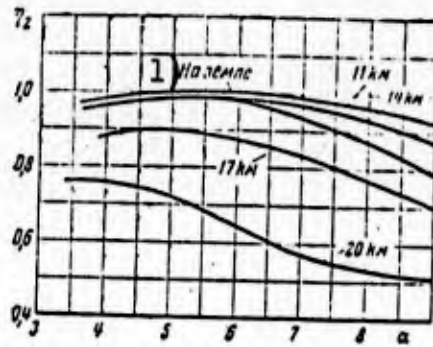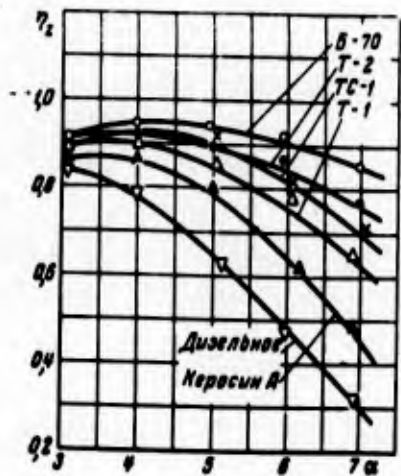
Fig. 82. Combustion-completeness curves for fuels of various fractional compositions as recorded in scaled-down combustion chamber. 1) B-70; 2) TS-1; 3) diesel; 4) kerosene A.

Fig. 83. Combustion-completeness characteristics for T-1 Fuel in VK-1 combustion chamber at various altitudes. 1) At surface.
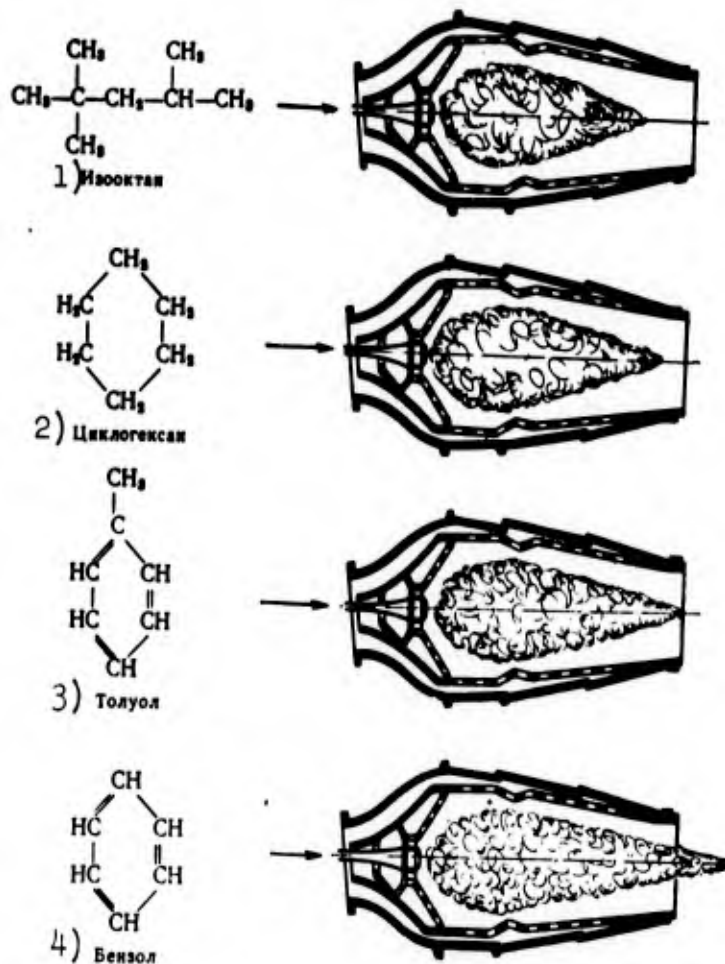
Fig. 84. Influence of chemical composition and structure of hydrocarbons on length of combustion flame. 1) Isooctane; 2) cyclohexane; 3) toluene; 4) benzene.

where η_z is the heat-evolution factor, $C_p t_z$ is the heat content of the combustion products, t_z is the average temperature of the gases at the exit from the combustion chamber, $C_p t$ is the heat content of the air at entry into the combustion chamber, t is the air temperature at the entry into the combustion chamber, G_b and G_m are the air and fuel flow rates.

The average temperature of the gases ($^{\circ}$K) at the combustion-chamber exit is

$$t_z = \frac{\Sigma t_i}{n},$$

where t_i is the local temperature in $^{\circ}$C and $\underline{n}$ is the number of points of the chamber.

The completeness of combustion η_z determined by this method as a function of fuel fractional composition and excess-air ratio α is shown in Fig. 82. The lighter the fractional composition, the higher will be the completeness of combustion.

A description of the completeness of combustion of T-1 fuel in the full-sized VK-1 turbojet chamber is shown in Fig. 83 for various altitudes.

A considerable drop in combustion completeness is observed at altitudes above 14 km.

The length of the combustion-products flame and the projection of this flame from the chamber represent a characteristic of completeness and stability of combustion as a function of fuel chemical composition (Fig. 84).

2. FORMATION OF CARBON IN COMBUSTION OF JET FUELS

In the combustion of hydrocarbon fuels, we observe deposition of disperse particles of carboniferous matter whose composition is close to that of carbon. The solid particles formed during combustion —

apparently as a result of pyrolysis of the fuel to coke — are carried away with the combustion products and may be visible in the form of smoke at high concentrations. Some of the coking products are deposited on the combustion-chamber surfaces, turbine blades, and other components. Carbon formation depends primarily on the conditions under which the fuel burns and its chemical composition, and particularly on the carbon and hydrogen contents. Further, carbon formation depends on a number of other factors:
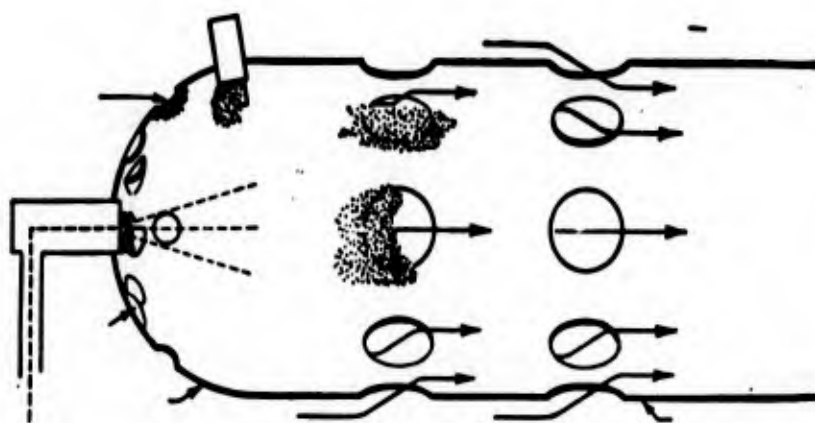
Fig. 85. Zones of carbon deposition in combustion chamber of turbojet engine.

1) the degree to which the fuel is atomized, which determines the conditions under which the combustible vapors are mixed with air;

2) the design of the combustion chamber;

3) the temperatures of the fuel and the air;

4) the surface tension and viscosity of the fuel;

5) the elementary composition of the fuel (content of aromatic hydrocarbons);

6) the excess-air ratio and the pressure at which combustion takes place.

In combustion of jet fuels, the carbon formed may be deposited on the nozzle or around the nozzle, and this may, in turn, result in
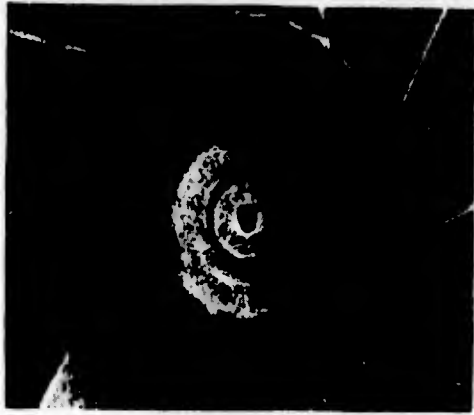
Fig. 86. Formation of carbon scale on nozzle bell of turbo-jet combustion chamber under test-stand conditions.

a change in the shape of the atomized spray; this will cause further carbon formation and a drop in combustion efficiency (Figs. 85, 86).

Carbon-scale deposits on the fire tubes of the combustion chamber and distortion of the atomized jet may result in local overheating, and, as a consequence of this, in deformation, cracking, and burnout of the combustion chamber. The carbon particles may progressively erode the turbine blades.

Carbon-scale formation is insignificant in contemporary engines, and it can be reduced to a minimum or virtually eliminated when the combustion process is well organized. Considerable attention is being
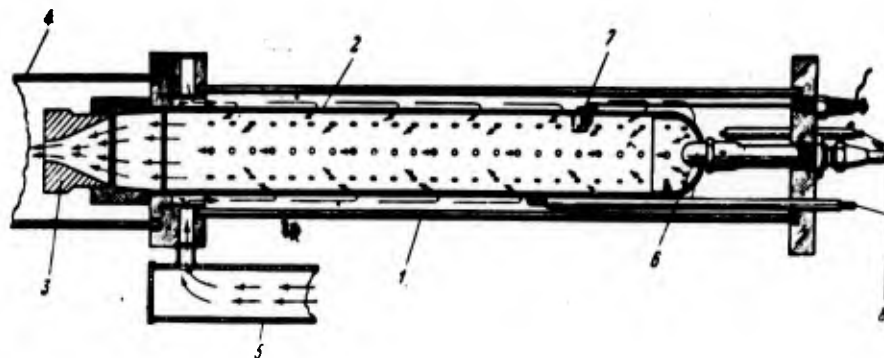
Fig. 87. Combustion chamber of laboratory test-stand air-breathing jet engine. 1) Shell of 75-millimeter quartz tubing; 2) 50-millimeter combustion chamber; 3) 12-millimeter nozzle; 4) quartz exhaust pipe; 5) air supply: pressure 3 atmospheres, temperature 120°; 6) fuel nozzle; 7) ignition; 8) thermocouples.

devoted to the carbon-scaling problem in connection with the use of fuels based on cracking products and the wide variety of engine designs in use. Below we shall consider the influence of fuel chemical composition on its tendency to form carbon deposits under comparable

experimental conditions.

Several research reports on scale formation by fuels as a function of their fractional and chemical composition have been published in the literature.

An interesting investigation in this direction was carried out by Ye. Starkman et al. [9] using a small laboratory-type combustion chamber. Figure 87 shows the working principle of this chamber.

The purpose of the investigations was to ascertain the influence of fuel chemical composition on the tendency of the fuel to carbon-scale formation. The following conditions were used in the tests:

Fuel feed, kg/hr...........................2.12

Air supply, kg/hr........................127.

Air:fuel ratio............................60:1

Duration of experiment, min..............15

Fuel-feed pressure, atmospheres..........10.3

Air-feed pressure, atmospheres............2.8

Duration of experiment, min..............15

Temperature of gases at nozzle exit, $^{\circ}C$ 650

The proportions by weight of air and fuel were varied from 60:1 to 75:1 and then to 120:1.

The combustion chamber was a sleeve 350 mm long with an outside diameter of 50 mm and a 1.6-mm wall thickness. Two hundred forty air holes 3.2 mm in diameter were made in the chamber surface. To permit observation of the combustion process, the chamber was placed inside a tube made from heat-resistant glass and 75 mm in diameter. The combustion chamber was weighed before and after the experiment and the amount of scale that had been deposited during the experiment was determined.

Table 76 presents data on the quantity of scale deposited on com-

bustion of various fuels and hydrocarbons. It depends on the chemical composition of the fuel (C/H ratio and volatility).

TABLE 76

Scale Deposition in Chamber of Air-Breathing Jet Engine During Combustion of Various Fuels and Hydrocarbons. Air:fuel ratio 60:1; duration of experiment 15 minutes.

1) Топливо	2) Т. кип., °C	3) Отношение С/Н	4) Отложение нагара, г
5) Авиационный бензин	62	6,8	0,19
6) Керосин	173	6,2	0,83
7) Гексан	65	6,0	8) Незначительное
9) Гептан	98	5,3	•
10) Изооктан	100	5,3	•
11) Изодекан	201	5,5	0,4
12) Циклогексан	80	6,0	0,45
13) Циклопентан	50	6,0	0,28
14) Бензол	80	12,0	1,64
15) Толуол	110	10,5	1,15
16) Кумол	154	9,0	1,71
17) Декалин	194	6,6	1,65
18) Тетралин	207	10,0	2,36
19) Метилнафталин	243	13,2	2,79

1) Fuel; 2) b.p., °C; 3) C/H ratio; 4) scale deposited, g; 5) aviation gasoline; 6) kerosene; 7) hexane; 8) insignificant; 9) heptane; 10) isooctane; 11) isodecane; 12) cyclohexane; 13) cyclopentane; 14) benzene; 15) toluene; 16) cumene; 17) decalin; 18) tetralin; 19) methylnaphthalene.

Carbon-scale formation depends on the boiling point of the hydrocarbon and its carbon content. The greatest tendency toward scaling is exhibited by the aromatic hydrocarbons, a lesser tendency by the naphthenes and the least by the paraffinic hydrocarbons. The tendency to carbon-scale formation can be represented by the following series:

aromatic hydrocarbon > aromatic hydrocarbons with side chains >
> naphthenes > olefins > paraffinic hydrocarbons.

Petroleum products occupy positions in this series in accordance with their group composition. However, scale formation is not an additive property.

An empirical equation linking the tendency of fuels to carbon scaling with the C/H ratio and boiling point of the hydrocarbons (and for petroleum products with their 10% distillation temperature) has been derived on the basis of experimental investigations:

$$W = \frac{\ln\left(\frac{C}{H} \cdot k_1 - k_2\right)}{k_3} + \frac{T}{k_4} - k_5,$$

where k_1, k_2, k_3, k_4, and k_5 are coefficients.

For the experimental chamber, this empirical equation assumes the following form with numerical coefficients:

$$W = \frac{\ln\left(\frac{C}{H} \cdot 0{,}83 - 1{,}5\right)}{0{,}54} + \frac{T}{225} - 3{,}0,$$

where T is the temperature (^{O}F).

Such empirical equations cannot be used to predict scaling in all cases, but they are suitable for comparative evaluation of the influence of fuel composition on scaling on the basis of C/H ratio and boiling point or fractional composition.
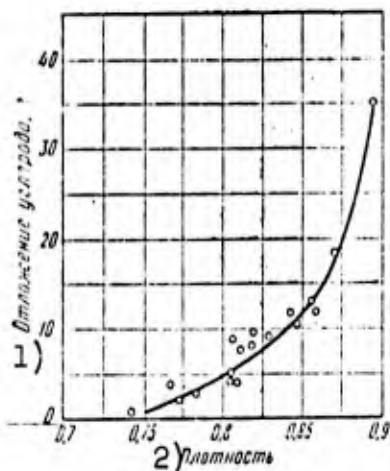
Fig. 88. Influence of fuel density on carbon-scale deposition in chamber of air-breathing jet engine. 1) Carbon deposit, g; 2) density.

The density of a fuel is related to its composition and boiling point, so that there is a relationship between scaling and fuel density. This relationship is presented in Fig. 88 in accordance with experimental data. Fuels with high densities possess stronger tendencies to scale formation.

The design of the combustion chamber, the temperature of the air fed into it, and the pressure under which combustion takes place exert an important influence on carbon-scale formation.

Scaling diminishes as the air temperature and the pressure at which combustion takes place in the chamber are raised. It is intensified as the air:fuel ratio diminishes.

In a one-hour scale-formation experiment with an air-to-fuel ratio of 50:1, using the chamber of an aviation engine under static-testing conditions, it was noted that the scaling is approximately directly proportional to the content of aromatic hydrocarbons in the fuel (Fig. 89). Thus, in tests of two aviation-kerosene specimens (of closely similar fractional compositions) containing 10 and 20% of aromatic hydrocarbons, the latter kerosene forms twice as much scale as the former. Scaling also increases with increasing boiling point of the fuel (Fig. 90). Aromatic hydrocarbons, which appear in fractions boiling above 200°, produce the heaviest scaling.
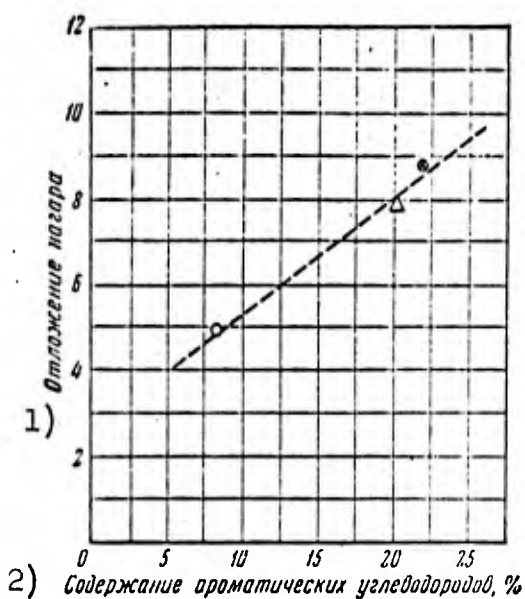
Fig. 89. Influence of aromatic hydrocarbon content in aviation fuel on scale deposit (in relative units). 1) Scale deposit; 2) aromatic-hydrocarbon content, %.
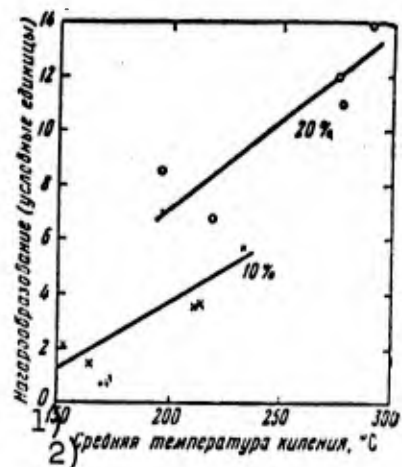
Fig. 90. Influence of mean boiling point of fuel on scaling for two fuels containing 10 and 20% of aromatic hydrocarbons. 1) Scaling (arbitrary units); 2) mean boiling point, °C.

Several types of fuels with predominant contents of various groups of hydrocarbons were also tested for scale deposition in the combustion chamber of a turbojet engine (Table 77).

TABLE 77

Deposition of Scale in Chamber of Turbo-
jet Engine as a Function of Fuel Group
Composition

1) Топливо	2) Групповой состав, %			6) Относи-тельное нагарооб-разование
	3) аромати-ческие	4) нафтены	5) парафины	
7) Авиационный керосин	19,4	39,2	41,4	100
8) Ароматическое топливо	75,2	11,4	13,4	700
9) Нафтеновое »	1,4	51,9	46,7	70
10) Парафиновое »	2,6	5,2	92,2	1

1) Fuel; 2) group composition, %; 3) aro-
matic; 4) naphthenic; 5) paraffinic;
6) relative scaling; 7) aviation kerosene;
8) aromatic fuel; 9) naphthenic fuel;
10) paraffinic fuel.

The data of Table 77 should be regarded as characterizing the

tendency of fuels of different group compositions to form scale.

The quantity of scale deposited depends on the mass of fuel

burned during the test, but it is not the same for fuels of different

natures. Figure 91 shows the quantity of scale deposited on the walls

of the experimental combustion chamber as a function of the quantity

of fuel burned and its nature [10].

Catalytic-cracking gasoil shows a higher level of scaling than

direct-distillation kerosene; this becomes particularly marked in long

experiments.

An interesting relationship was noted between the scaling ten-

dency of the fuels in a jet-engine chamber and their ability to burn

in air on the wick of a diffusion burner with liberation of carbon.

In this case, the technique of evaluating the quality of illuminating

kerosenes and the hydrocarbons that form them reduces to determina-

tion of the maximum smokeless-flame height [11]. The working principle

of such a device is shown in Fig. 92.

Thus, we observe the following relationship between aromatic
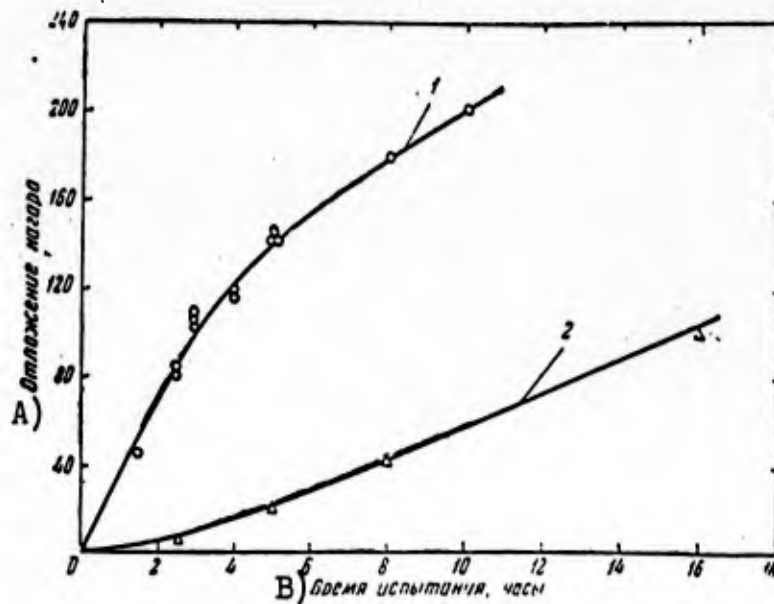
Fig. 91. Influence of nature of fuel on carbon deposition (in relative units) in experimental combustion chamber. 1) Catalytic-cracking gasoil (contains 32% of aromatic hydrocarbons); 2) kerosene (contains 15% of aromatic hydrocarbons); A) deposition of scale; B) test time, hours.

hydrocarbon content and maximum smokeless-flame height for the kerosenes [12].

Aromatic-hydrocarbon content, %	10	18	22	28
Maximum smokeless-flame height, mm	23	19	14	12

A characterization of the tendency of fuels to scaling on the basis of the smokeless-flame height has recently appeared in the technical specifications for turbojet fuels such as JP-5.

The influence of the chemical structure of the hydrocarbons and the number of carbon atoms in the molecule on the maximum rate of fuel consumption on a burner wick without smoking is shown in Fig. 93 [13].

Other laboratory methods for characterizing the tendency of fuels to scaling are also of interest.

The author investigated carbon-scaling by fuels using the laboratory combustion chamber the working principle of which has already been described.

During combustion of 2-3 g of fuel, the carbon liberated was deposited on the nozzle section of the combustion chamber, which was then weighed on an analytical balance to within 0.1 mg, and the quantity of deposit formed was reduced to 1 kg of fuel burned. This method of evaluating scale formation is distinguished by high accuracy and good reproducibility.

As determined by this method, the scaling values for hydrocarbons having approximately the same boiling point are as follows [8]:

	mg/g
benzene	2.80
cyclohexane	0.70
cyclohexene	1.30
heptane	0.40

Apart from its absolute value, scaling is also expressed in relative units, taking the scaling of benzene as unity (Table 78).

The relative scaling values determined by the different methods agree well for the various hydrocarbons.

The influence exerted on scaling by small amounts of fuel additives was studied simultaneously.

The influence of certain additives — designated arbitrarily by A and B (1-2%) on scaling (in mg of deposit per 1 g of fuel burned) is shown in Fig. 94. Thus, the scaling of fuels with high aromatic hydrocarbon contents can be reduced by additives [8].

Data on the influence of additives on fuel combustion in gas turbines are extremely scanty.

Thus, in the middle of 1953, a report [14, 15] appeared on the possibility of raising the combustion efficiency of fuels with high aromatic-hydrocarbon and sulfur-compound contents by the use of peroxide and nitrate additives to the fuel. Hydrocarbon hydroperoxides added to the fuel in quantities from 0.1 to 5% were suggested as additives.
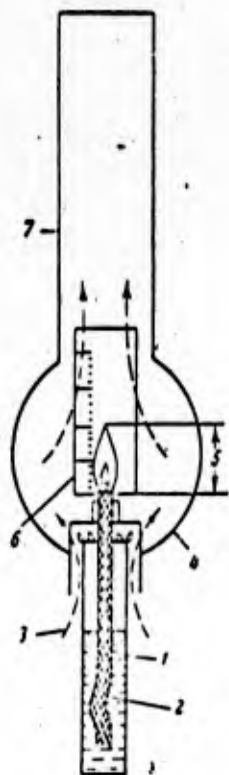
Fig. 92. Burner for defi-
nition of tendency of
fuels to scale by smoking
criterion. 1) Fuel; 2)
wick; 3) air influx; 4)
combustion chamber; 5)
flame-height measurement;
6) scale; 7) lamp chimney.
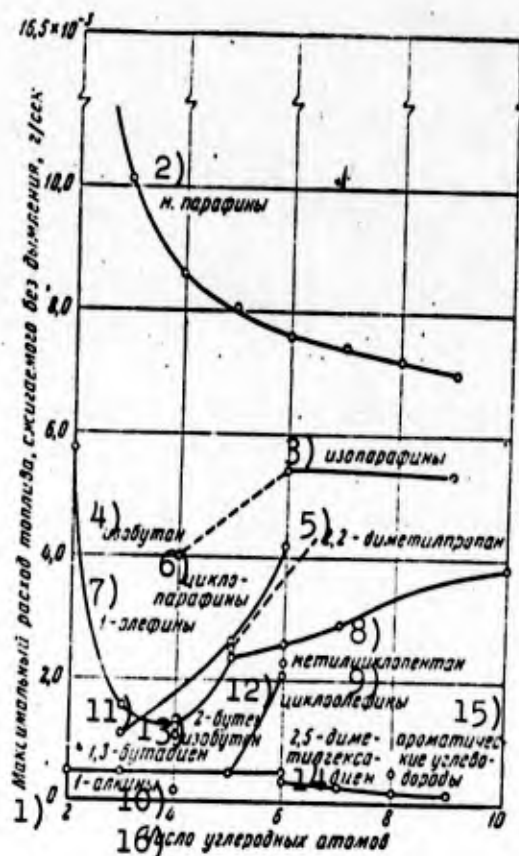
Fig. 93. Influence of chemical structure
of hydrocarbons and number of carbon
atoms in molecule on maximum fuel con-
sumption rate on lamp wick without
smoking. 1) Maximum fuel consumption
rate without smoking; g/sec; 2) normal
paraffins; 3) isoparaffins; 4) iso-
butane; 5) 2,2-dimethylpropane; 6) cyclo-
paraffins; 7) 1-olefins; 8) methylcyclo-
pentane; 9) cycloolefins; 10) 1-alkynes;
11) 1,3-butadiene; 12) 2-butene; 13) iso-
butene; 14) 2,5-dimethylhexadiene; 15)
aromatic hydrocarbons; 16) number of
carbon atoms.

Thus, 52.6 g of deposit were obtained in tests of an experimental

fuel sample containing 99% of aromatic hydrocarbons, while after

addition of 2% of cumene hydroperoxide, only 19.9 g of scale was

formed, i.e., scaling had been reduced by more than half [14].

It has also been suggested that ammonium nitrate be used to raise

the combustion efficiency of gas-turbine fuels. Aqueous solutions

of ammonium nitrate are injected into the combustion chambers of com-

mercial gas turbines for this purpose [15].

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Fig. 94. Variation of scaling as a function of
aromatic-hydrocarbon content in fuel and addi-
tives to fuel. 1) Without additives; 2) additive
A; 3) additive B. a) Scaling, mg/g; b) aromatic-
hydrocarbon content, %.

TABLE 78

Comparative Data on Relative Scale Formation

	1) Горючее	2) Относительное нагарообразование	
		3) лабораторная камера [8]	4) двигатель Таркмана [9]
5)	Бензол	1,0	1,0
6)	Циклогексан	0,23	0,3
7)	Изооктан	0,07	—
8)	Изопропилбензол.	1,04	1,01
9)	Керосин	0,6	0,52
10)	Дизельное топливо	1,1	1,09

1) Combustible; 2) relative scale formation;
3) laboratory chamber [8]; 4) Starkman engine;
[9]; 5) benzene; 6) cyclohexane; 7) isooctane;
8) isopropylbenzene; 9) kerosene; 10) diesel
fuel.

Like the completeness of fuel combustion, scaling depends on

the chemical and fractional compositions of the fuel. Optimum engine

designs and operating modes in which these phenomena may not appear

or will be reduced to a minimum can be found. Even then, however, it

is necessary to reckon with incomplete combustion and scaling if it

becomes necessary to use lower-quality fuel, and on transition to

stressed engine-operating conditions [16].

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Manu-script Page No.	[Footnotes]
253	*At high flight speeds (2400-3000 km/hr), the fuel tanks may be heated to 120-200°, and some of the fuel may vaporize and enter the engine in vapor form.

Manu-script Page No.	[List of Transliterated Symbols]
244	Φ = f = fakticheskiy = actual
244	H = n = nizshiy = lower-limit
249	уд = ud = udel'nyy = specific
249	T = t = toplivo = fuel

Chapter 7
IGNITION PROPERTIES OF REACTION FUELS

1. General Data

The ignition of the vapors of a vaporized fuel at atmospheric pressure is accomplished easily by means of an electric spark plug. To start turbojet engines, aviation gasoline is employed, because it provides for good ignition under all operating temperature conditions, including temperatures as low as -50°. Apparently, fuels of expanded fractional composition can be employed for the starting of engines, since they contain gasoline fractions. A fuel of the aviation-kerosene type does not provide for reliable starting at temperatures of the order of $-30-40^{\circ}$, although a fuel of this type, at standard temperature, ignites well.

However, the starting of turbojet engines at altitudes above 10 km, at a temperature of below -55° for the ambient medium, and at reduced pressures, involves considerable difficulties in view of the fact that under such conditions hydrocarbon fuels are considerably harder to ignite and the initial combustion is somewhat too sluggish and does not exhibit adequate intensity to ignite the basic fuel. The starting of a turbojet engine prior to flight is carried out on the ground, i.e., under favorable conditions. However, it may become necessary to restart an engine during flight; this may occur, for example, in the case of flameout or the forced stoppage of an engine; and it may also occur in the case in which only a part of the engines of a multiengine turbojet aircraft are functioning and it becomes necessary

at a specific instant of time under high-altitude flight conditions to start the remaining engines.

Thus the study of the relationship between the composition of fuels and their ignition and starting characteristics, as well as the possible development of special starter fuels for specific applications, are matters of great urgency.

In the case of turbojet engines, by "starting characteristics" of a fuel we mean the capacity of a fuel to be ignited by means of an electric spark plug in the starter injector and the possibility of bringing the engine to its operational regime by means of the fuel which is used for starting purposes (the fuel may be a starter or basic fuel). In this case, the starter fuel must provide for sufficiently stable and intensive combustion after ignition in order to ensure the ignition of the basic fuel portion. Thus the following requirements could be imposed on a TRD [turbojet engine] fuel:

a) the capacity to ignite at altitudes of 10-25 km at pressures of 0.05-0.25 atm and at temperatures above -55°;

b) the capacity to burn stably at pressures of 0.05-0.25 atm;

c) combustion intensity at pressures of 0.05-0.25 atm, adequate to ensure the ignition of the basic fuel.

Some of these requirements can probably be resolved by physicomechanical means (fuel vaporization, mixing). But all other conditions being equal, the chemical nature of the fuel will determine whether or not these above-mentioned requirements are satisfied.

The starting properties of a fuel are determined by a complex of physicochemical phenomena. The possibility of igniting fuel vapors in a mixture with air is determined by:

1) the concentration limits of fuel ignition in air;

2) the minimum fuel-air-mixture pressure at which ignition is pos-

sible;

3) the minimum energy required for the ignition of the combustible mixture (the energy of the electric spark);

4) the temperature required for the self-ignition of the fuel vapors mixed with air;

5) ignition lag;

6) the possibility of propagating the flame through the combustible mixture;

7) the degree of fuel vaporization;

8) fuel volatility;

9) temperature conditions and the velocity of the air.

In addition, ignition is determined by a number of other physical and chemical factors, as well as the construction and power of the ignition source.

The role of the ignition processes is not restricted to the initial instants of engine ignition, but exerts an effect throughout the entire fuel-burning regime. The fuel-burning process involves the entire period of time from the instant of ignition to the formation of the final products of combustion. It is for this reason that fuel ignition is regarded as one of the stages of burning.

2. Ignition Limits [1-5]

The ignition of fuel vapors by means of an electric spark is a complex physicochemical process which, as is well known, is characterized by the concentration limits of fuel ignition which are functions of the chemical composition of the fuel. For example, for a number of substances these limits have the following values [1] (in terms of the weight ratio between air and fuel):

	Rich mixture	Lean mixture
Heptane............................	4.5	27.4
Cyclohexane.....................	3.9	24.5
Benzene.........................	5.2	25
Ethylene........................	5.3	55
Aviation kerosene.............	5	25

The stoichiometric ratio of the combustible (fuel) mixture, i.e., air-to-fuel, is approximately equal to 15. The widest ignition limits are observed in the case of compounds that are unsaturated in nature — ethylene and acetylene. Paraffinic, naphthenic and aromatic hydrocarbons, as well as olefins, boiling over within the same range as the gasolines, exhibit a narrow ignition range (close ignition limits).

In a turbine, the fuel mixture ratio (taking into consideration the secondary air), in the opinion of many authors, may range from 50:1 to 100:1 and higher. However, in the combustion chamber and in the starter injector these ratios are close to the stoichiometric, although we can assume that even here deviations are possible, depending on the quantity of secondary air.

The limits of ignition change as a function of the power of the spark pulse, the temperature of the air-vapor mixture, and the pressure under which the mixture is kept.

Figure 95 shows the ignition limits for the vapors of three combustibles as a function of the excess-air ratio and pressure [2].

Acetylene and propylene oxide ignite at comparatively lower pressures and within a wider range of concentrations than do the paraffinic hydrocarbons.

The effect of the molecular weight of the paraffinic hydrocarbons C_1-C_7 on the ignition limits at low pressures is shown in Figs. 96 and 97. The ignition range expands with an increase in the molecular weight
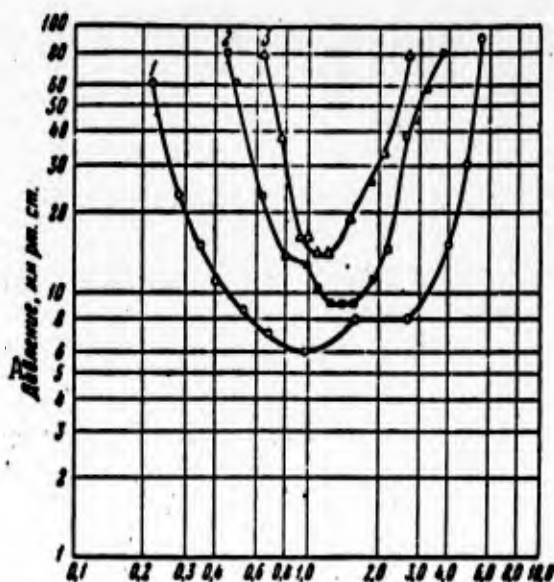
Fig. 95. Limits of ignition by means
of electrical spark for various com-
bustibles at low pressures. 1) Ace-
tylene; 2) propylene oxide; 3) iso-
pentane; A) pressure, mm Hg. The ex-
cess-air ratio has been plotted along
the axis of abscissas.

of the hydrocarbons. A study has also been undertaken of the effect

that a normal and branched chain has on the ignition range; it turned

out that the ignition range for n. paraffins and isoparaffins is vir-

tually identical.

3. Minimum Critical Ignition Energy

In addition to the concentration ignition limits, the capa ˙ty of

the combustible mixture to ignite is characterized by the minimum en-

ergy of the electric spark which produces the ignition. Not every

spark, in ˙ping through the combustible mixture, causes the ignition

of the mixture, although the temperature of such a spark attains thou-

sands of degrees. A certain minimum spark-discharge energy is required

in order for ignition to take place and to produce a self-propagating

combustion reaction; this minimum energy is a function of the chemical

composition of the fuel as well as of temperature and pressure. The

energy of the spark discharge is generally expressed in millijoules.

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Figure 98 shows the effect of temperature and pressure on the minimum ignition energy of an electric spark in the case of propane-air mixtures. The minimum spark energy for ignition, when pressure is reduced from 1 to 0.2 atm, increases by a factor of almost ten.

The magnitude of the critical ignition energy for a spark employed to ignite mixtures of various compositions ranging from methane to heptane, at atmospheric pressure, is presented in Fig. 99. The higher hydrocarbons (between C_5 and C_7) yield a wider ignition range for lower critical spark energies [3, 4].
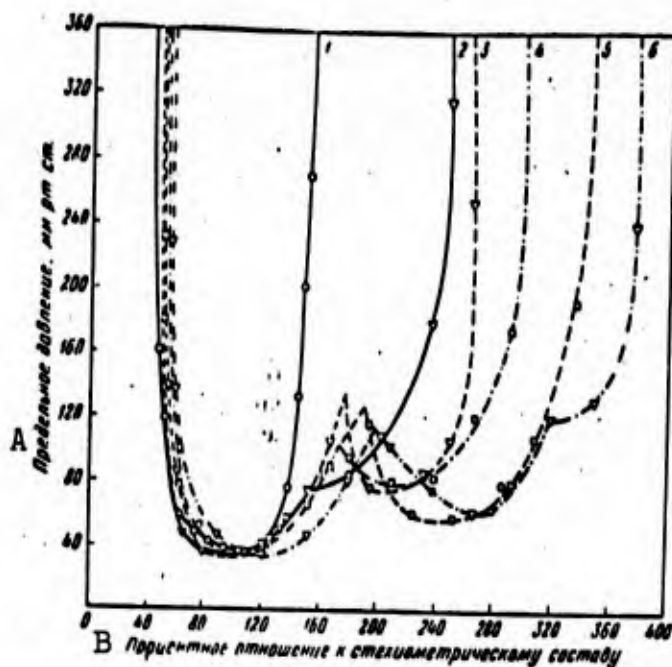
Fig. 96. Effect of molecular weight of hydrocarbons on ignition range. 1) Methane; 2) ethane; 3) propane; 4) butane; 5) pentane; 6) hexane. A) Maximum pressure, mm Hg; B) percentage ratio to stoichiometric composition.

The minimum spark energy required for the ignition of unsaturated compounds is lower than that required for saturated compounds and is a function of the degree of saturation. Figure 100 shows the magnitudes of this energy for various stoichiometric mixture ratios, and Fig. 101 shows the magnitude of energy for various hydrocarbons containing
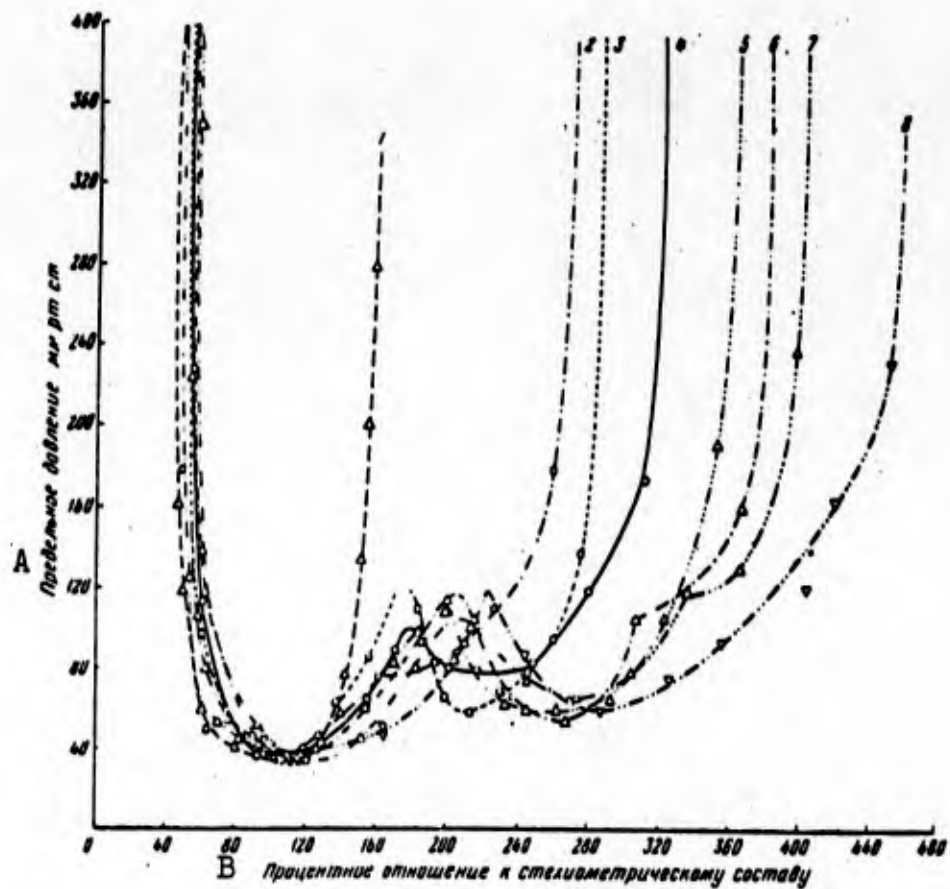
Fig. 97. Effect of molecular weight of hydrocarbons
on ignition range. 1) Methane; 2) ethane; 3) 2,2-
dimethylpropane; 4) butane; 5) pentane; 6) 2-meth-
ylpentane; 7) hexane; 8) heptane. A) Maximum pres-
sure, mm Hg; B) percentage ratio to stoichiometric
composition.
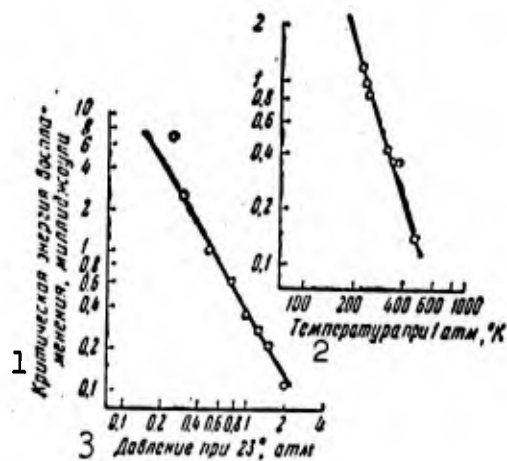
Fig. 98. Effect of temperature
and pressure on critical igni-
tion energy for a propane-air
mixture. 1) Critical ignition
energy, millijoules; 2) tempera-
ture, at 1 atm, $^{\circ}K$; 3) pres-
sure, at 23°, atm.
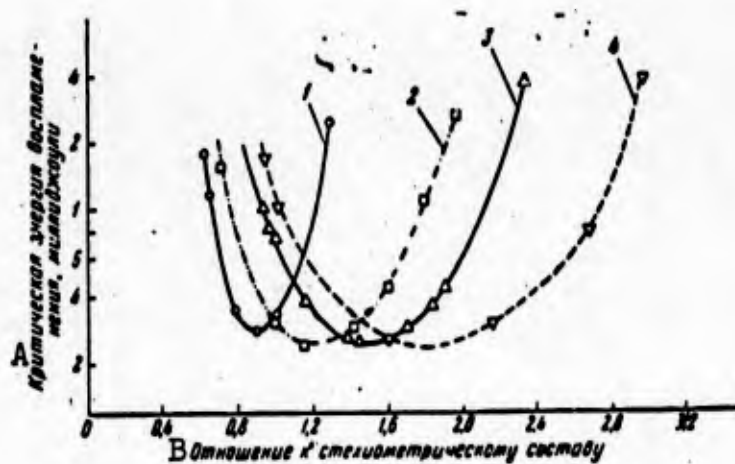
Fig. 99. Effect of molecular weight and composition of mixture on critical ignition energy produced by electric spark. 1) Methane; 2) ethane; 3) butane; 4) heptane. A) Critical ignition energy, millijoules; B) ratio to stoichiometric composition.

double and triple bonds, as well as for hydrocarbons having carbon atoms of various skeletal structures.

The minimum ignition energy for hydrocarbons characterizes not only the ability of the hydrocarbons to ignite, but the behavior of the hydrocarbons during the operating regime, and this will be shown in the following chapter.

4. Self-Ignition Temperature

The self-ignition temperature is that temperature at which the self ignition of a mixture of fuel vapors with air takes place without contact with an open flame. The conditions of self ignition are associated with the liberation of heat in a preflame reaction (for the left-hand part of the equation, see below) and the removal of heat to the ambient medium (for the right-hand part of the equation, see page 372):

$$v \cdot A \cdot \iota^n \cdot e^{-\frac{E}{RT}} > \alpha (T_1 - T_0) F.$$

Thus the self-ignition temperature is not a physical constant but a function of the conditions of the experiment: of the volume and sur-

face of the reaction vessel, of pressure, the conditions of heat transfer, etc.

We may expect that the lower the self-ignition temperature for the vapor fuels mixed with air, the more rapid the onset of the self-ignition process for the mixture.

Fig. 100. Effect of degree of hydrocarbon saturation on critical electric-spark ignition energy for combustible mixture. 1) Ethane; 2) ethylene; 3) acetylene. A) Critical ignition energy, millijoules; B) ratio to stoichiometric composition.
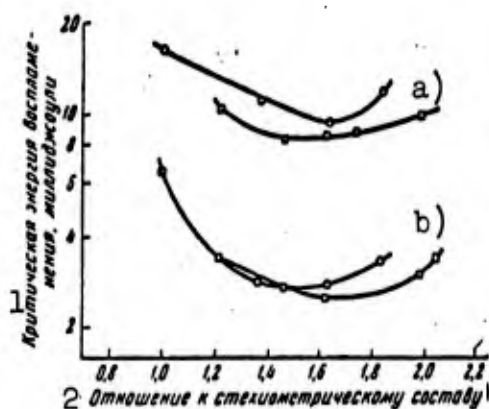
Fig. 101. Effect of chain branching on critical ignition energy. o) 2,2-Dimethylbutane; □) hexane; a) pressure, 100 mm Hg; b) pressure, 200 mm Hg. 1) Critical ignition energy, millijoules; 2) ratio to stoichiometric composition.

Ignition by means of an open flame is different from self ignition,
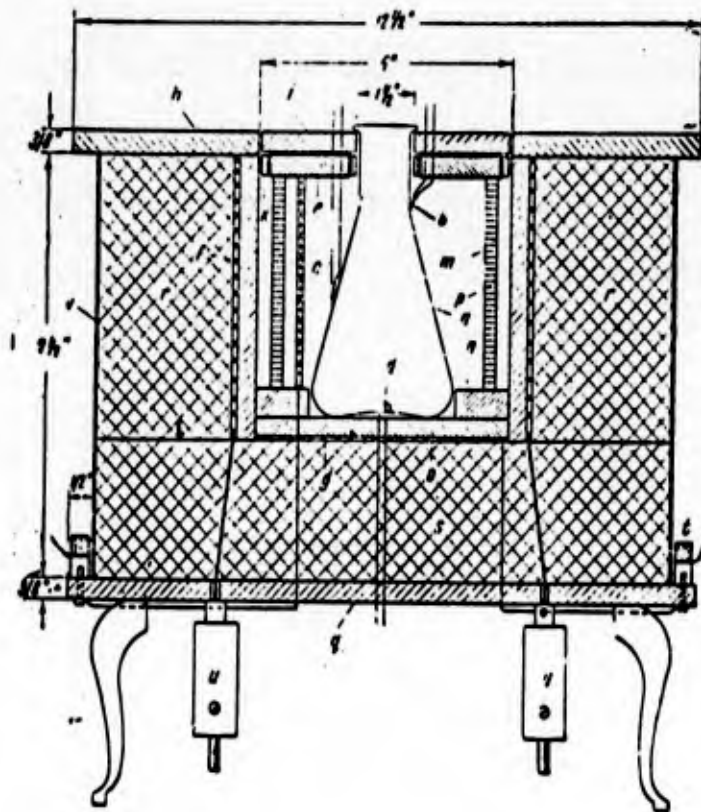
Fig. 102. Device for determination of self-ignition temperature. a) Quartz flask, in which the test is carried out; b, c, d) thermocouples; p) furnace; f, g) electric heaters; e, h, and i) covers; o and n) supports; r and s) heat insulation; v) shell; q) furnace support; t and u) contacts.

because in the case of contact with an open flame there is transfer of heat and of the active centers from the temperature zones between 1500 and 3000°. However, a common denominator for self ignition and contact ignition is the presence and development of preflame reactions, no matter that they last but extremely short periods of time.

In connection with the extensive use of hydrocarbon fuels in engines in which ignition is accomplished by compression, a rather large number of investigations have been devoted to a study of the temperature of hydrocarbon self-ignition as a function of structure. The self-ignition temperature for diesel fuels determines their most important characteristic — starting properties. For jet fuels, this characteristic is not completely clear, but it may be taken into consideration.
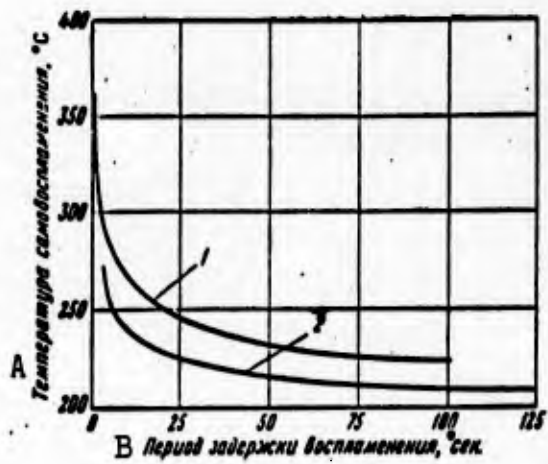
Fig. 103. Self-ignition lag as a function of temperature for heptane and decane. 1) n. heptane; 2) n. decane. A) Temperature of self ignition, °C; B) ignition lag, sec.
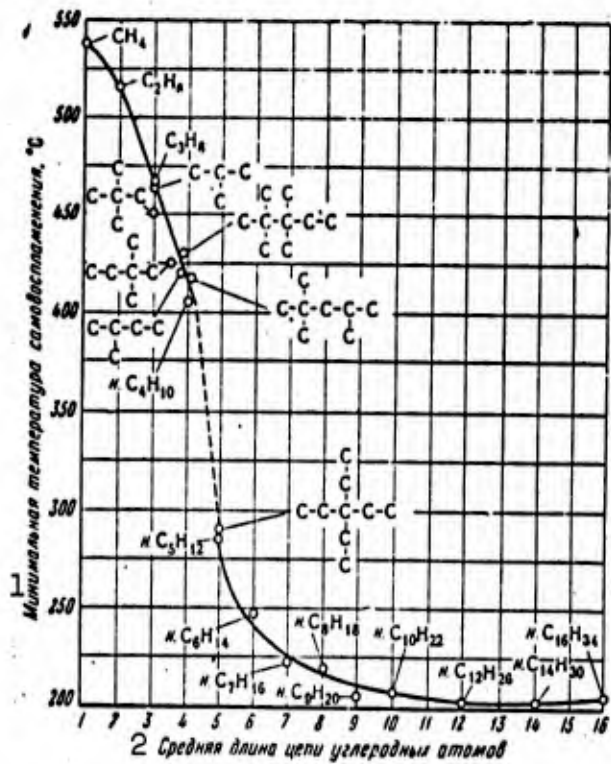
Fig. 104. Minimum self-ignition temperature as a function of the structure of paraffinic hydrocarbons. 1) Minimum self-ignition temperature, °C; 2) average length of carbon-atom chain.

In one project, carried out in 1954 [4], the self-ignition temperature was determined in the device shown in Fig. 102. In principle,

TABLE 79

Minimum Self-Ignition Temperatures and Self-Ignition Lags for Hydrocarbons and Fuels in Air, at Atmospheric Pressure [4, 5]

1 Вещество	2 Температура самовоспламенения, °C	3 Период задержки самовоспламенения, сек.
Этан	515	10
и. Бутан	405	6
и. Пентан	287	10
и. Гексан	234	57
и. Гептан	223	101
и. Октан	220	132
и. Нонан	206	130
Изооктан	418	27
и. Декан	208	124
и. Гексадекан	205	141
Циклогексан	200	206
Бензол	562	32
Толуол	536	72
м-Ксилол	528	61
Нафталин	526	18
α-Метилнафталин	529	23
Антрацен	540	17
Керосин	229	210
Авиационный бензин 100/130	440	—
Реактивные топлива:		
JP-1	228	120
JP-3	238	187
JP-4	242	185

1) Substance; 2) self-ignition temperature, °C; 3) self-ignttion lag, sec; 4) ethane; 5) n. butane; 6) n. pentane; 7) n. hexane; 8) n. heptane; 9) n. octane; 10) n. nonane; 11) iso-octane; 12) n. decane; 13) n. hexadecane; 14) cyclohexane; 15) benzene; 16) toluene; 17) m-xylene; 18) naphthalene; 19) α-methylnaphthalene; 20) anthracene; 21) kerosene; 22) aviation gasoline 100/130; 23) jet fuels.

the method involves the introduction of 1 ml of the substance being investigated into a special quartz vessel heated to a certain temperature by means of a special furnace, and the recording of the self-ignition lag. The relationship between the temperature and the magnitude of the self-ignition lag corresponding to this temperature for n. heptane and n. decane in air at atmospheric pressure is shown in Fig.

103. For heptane the minimum self-ignition lag corresponds to 223°
with an induction period of 101 seconds, and self ignition takes place
at 370° with a lag that is faster than the eye (about 0.1 sec). This
temperature corresponds to a higher self-ignition temperature.

Figure 104 presents the lower self-ignition temperature for
paraffinic hydrocarbons as a function of the number of carbon atoms
and structure.
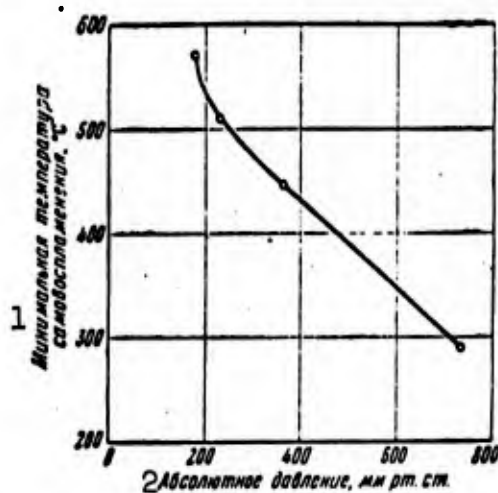
Fig. 105. Effect of pressure
on minimum self-ignition tem-
perature for jet fuel JP-4. 1)
Minimum self-ignition tempera-
ture, °C; 2) absolute pressure,
mm Hg.

The lower self-ignition temperature for paraffinic hydrocarbons
in air diminishes as molecular weight increases. In this connection,
there is an analogy between the change in the critical electric-spark
ignition energy and the concentration ignition range which expands
from methane to heptane.

Isoparaffins have higher self-ignition temperatures in comparison
with normal paraffins of the same molecular weight [5].

Table 79 presents the self-ignition temperatures for a number of
hydrocarbons.

Pressure also has a substantial effect on the minimum self-

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TABLE 80

Minimum Self-Ignition Temperature
for Fuels ($^\circ$C) in Air as a Function
of Pressure [4]

1 Топливо	2 Давление 370 мм	3 Давление 742 мм
4 Авиационные топлива.		
JP-4	444	242
JP-3	440	238
JP-1	462	228
5 Авиационный бензин 100/130 . . .	553	440
6 н. Декан	458	208
7 н. Октан	465	220
8 н. Гексан	497	234

1) Fuel; 2) pressure, 370 mm; 3)
pressure, 742 mm; 4) aviation fuels;
5) aviation gasoline 100/130; 6) n.
decane; 7) n. octane; 8) n. hexane.

ignition temperature, as was demonstrated in Reference [4].

Figure 105 shows the effect of air pressure on the minimum self-
ignition temperature of the JP-4 turbojet fuel. With a drop in pres-
sure by a factor of approximately three, the self-ignition tempera-
ture increased by a factor of two.

Table 80 shows the effect of pressure on the self-ignition tem-
perature of a number of fuels.

In all fuels, the self-ignition temperature increases as pres-
sure diminishes. However, this change depends on the nature of the
fuel and is most pronounced in the case of heavy fuels.

Figure 106 shows the change in the self-ignition temperature of a
number of combustibles at atmospheric pressure as a function of chem-
ical composition for various induction periods. In oxygen the same
quantitative relationships for the self-ignition temperature are ob-
served as in the case of air.

The fuel ignition process which takes place under the action of
high temperatures can be characterized by a self-ignition lag for a

given temperature and pressure (Fig. 107). The self-ignition lags for various hydrocarbons are determined in a bomb at a temperature of 582° and a pressure of 21.4 atm. The self-ignition lags under these conditions increase for a number of n. paraffins, olefins, and naphthenes [3].
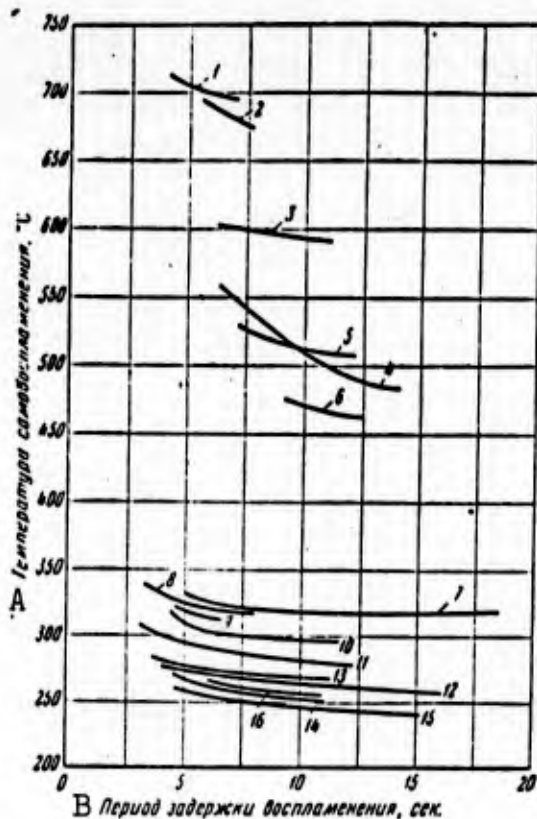
Fig. 106. Self-ignition temperature and lag for a number of hydrocarbons in air. 1) Benzene; 2) toluene; 3) o-xylene; 4) 1,2,3-trimethylbenzene (hemimellitol); 5) 1-ethyl-2,4-dimethylbenzene; 6) 1-ethyl-2,3-dimethylbenzene; 7) methylcyclohexane; 8) 1,1,3-trimethylcyclopentane; 9) trans-1,3-dimethylcyclohexane; 10) ethylcyclohexane; 11) n. propylcyclopentane; 12) n. heptane; 13) n. octane; 14) n. decane; 15) n. dodecane; 16) n. tetradecane. A) Self-ignition temperature, °C; B) ignition lag, sec.

The self-ignition lags for aromatic and paraffinic hydrocarbons, as well as for diesel fuel in a bomb, are presented in Fig. 108 for various temperatures. The self-ignition lags for diesel and jet fuels

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in a temperature range from 455 to 570° lie between the ignition lags for paraffinic and aromatic hydrocarbons: the smallest self-ignition lags pertain to the paraffinic hydrocarbons and the greatest pertain to the aromatic hydrocarbons.

Thus the ignition of a mixture of fuel vapors with air is characterized by a series of parameters such as: the concentration ignition range at atmospheric pressure, the concentration ignition range at reduced pressures, the minimum critical energy of the spark discharge required for the ignition of the vapor-air mixture, the self-ignition temperature, the self-ignition lag, etc.

These parameters are determined by the chemical properties which are most favorable in the case of paraffinic hydrocarbons with great molecular weight. A wide ignition range is exhibited by the lower highly unsaturated hydrocarbons.

The investigations carried out on the hypergolic properties of kerosene drops in a stream of air heated to a high temperature are extremely interesting [6]. With an increased temperature between 850 to 950° the self-ignition lag for a 55-μ drop diminishes by a factor of approximately five. The dimensions of the drops also affect the self-ignition properties. For example, 140-μ drops self-ignite at 970° with a lag that is 30% greater than for drops having dimensions of 55 μ. The total burning time for the fuel drops in the stream of air is composed of the ignition lag and the burning time. Figure 109 shows the change in ignition lag and burning time for kerosene drops having dimensions of 70 μ at various temperatures. The time of the actual burning process is greater by a factor of approximately 3-4 than the self-ignition lag.

The pressure whose effect was investigated for a pressure range from 0.3 to 1.0 atm (Fig. 110) has a pronounced effect on the ignition

of kerosene drops. With a change in the pressure from 0.3 to 1.0 atm, the self-ignition lag at 900-1000° changes by a factor of approximately 3.

Fig. 107. Ignition lag for hy-
drocarbons in a bomb at 582°
and 21.1 atm. 1) Ignition lag,
sec; 2) number of carbon atoms;
3) decalin; 4) cyclohexanes;
5) dicyclohexyl; 6) α-olefins;
7) n. paraffins.

Under practical operating conditions, good fuel oxidizability may be extremely important. In the case of metal-organic fuels (compounds of aluminum and boron) start and combustion is possible to altitudes of 25-30 km, and in the case of hydrocarbon fuels — to 15-22 km [7].

The light hydrocarbons of aviation gasoline exhibit adequate vapor tension at temperatures of −40 to 60°. Therefore, aviation gaso-line provides for good engine starts under all temperature conditions. It is possible that the vapors of the hydrocarbons which have molecular weights that place them in the boiling range of kerosene (C_{10}-C_{16}) must exhibit better ignition characteristics than those in the boiling range of gasoline (C_5-C_9). But the conversion of the former into a vapor phase at the temperature of the ambient medium under high-alti-

- 295 -
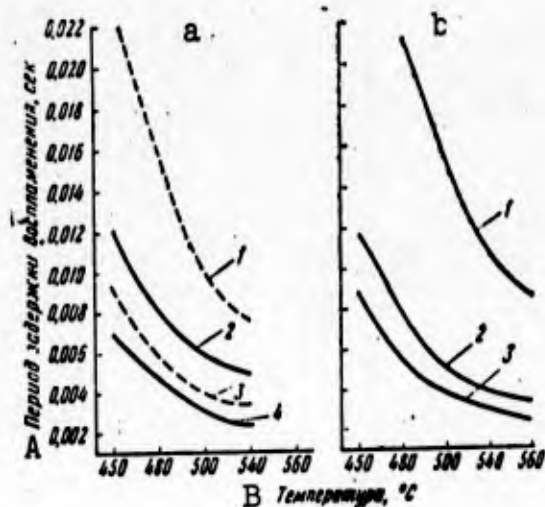
Fig. 108. Self-ignition lag for hydrocarbons and fuels as a function of temperature. a) Pressure, 21.1 kgf/cm^2; 1) isooctane; 2) n. octane; 3) octadecene-1; 4) n. octadecane; b) pressure, 36.9 kgf/cm^2; 1) aromatic fraction of fuel; 2) diesel fraction; 3) paraffinic-naphthenic fraction. A) Ignition lag, sec; B) temperature, ^oC.

tude conditions, with the required concentration, is difficult without heating of the combustible mixture.

There is no doubt that the chemical nature of the fuel is extremely important in the burning process, since this determines the ignition characteristics of the fuel vapors as they encounter the flame front. However, the following physical parameters are also important here: fuel volatility, fuel vaporization and mixing; under certain conditions these can be of greater significance than the chemical parameters. On the whole, the entire process is limited by the stage which takes place at the least relative rate.

In the case of turbojet engines of conventional type, the start of an engine operating on petroleum fuels under ground and flight conditions to altitudes of 10 km is determined primarily by the following physicomechanical factors: fuel volatility and the degree of fuel vaporization. The latter is a function of viscosity and the surface

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tension of the fuel, as well as of the vaporization system employed (the type of spray nozzles) and feed pressure.

There are indications in the literature that at a viscosity above 15 centistokes good fuel vaporization into the engine is no longer assured. However, at low temperatures, a viscosity of up to 25 centistokes is technically permitted for a turbojet fuel. It has been established experimentally that gas oil having a viscosity of 15 centistokes (at 20°) fails completely to provide the required vaporization for starting at temperatures below -7°. However, kerosene with a viscosity of 3-4 centistokes (at 20°) continues to provide satisfactory vaporizations at temperatures of -40 and -60°. Gasolines provide good vaporization at all temperatures.
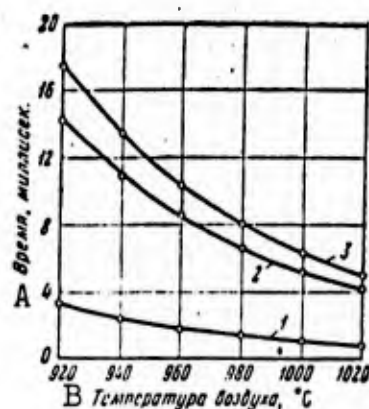
Fig. 109. Effect of temperature on self-ignition lag and burning time for drops of kerosene having dimensions of 70 μ in a stream of heated air. 1) Self-ignition lag; 2) burning time; 3) total burning time. A) Time, milliseconds; B) air temperature, $^{\circ}C$.

The ease of engine start is a function of fuel volatility. Volatility and, consequently, ease of VRD start is characterized by the temperature at which 10% of the fuel boils off. The 10%-distillation temperature for the majority of air-reaction-engine fuels such as kero-
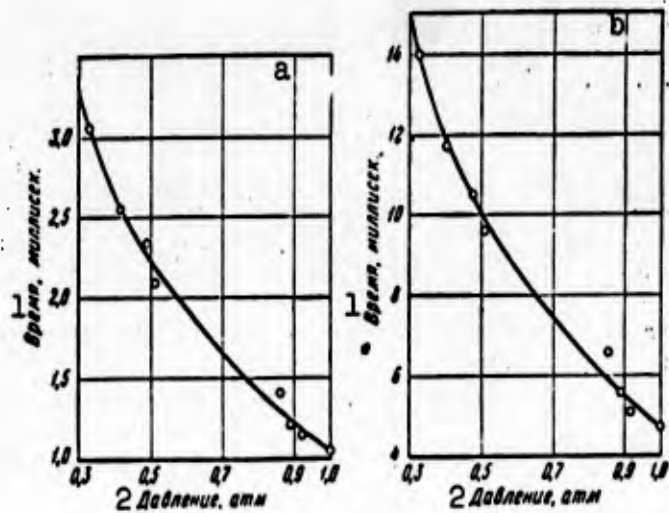
Fig. 110. Effect of pressure on self-ignition lag for kerosene drops in a stream of heated air. a) Air temperature, 1000°; b) air temperature, 900°. 1) Time, milliseconds; 2) pressure, atm.

sene has a value of the order of 175-210°. The lower the 10%-distillation temperature, the easier the start and the lower the feed pressure can be.

For example, engine start was impossible with a gas oil having a boiling range between 240-365°, although the engine could operate on this fuel if it had been started in advance with kerosene. With heavier gas oil (boiling range 256-396°) the engine was completely incapable of operation. Gasoline-free petroleum with a boiling range of 207-400° could be used in an engine if it were first started with kerosene. However, in this case unstable engine operation was observed throughout the entire velocity range [8].

Aviation gasoline with a 10%-distillation temperature of 71° provides for ease of engine start at temperatures to −55-60°. When using fuels having a 10%-distillation temperature of 190°, engine starts at −40° are difficult.

During starting, a low-volatility fuel may partially be deposited in a drop-liquid state on the walls of the engine, causing a lag in ignition. As a result, there will be an accumulation of fuel which will
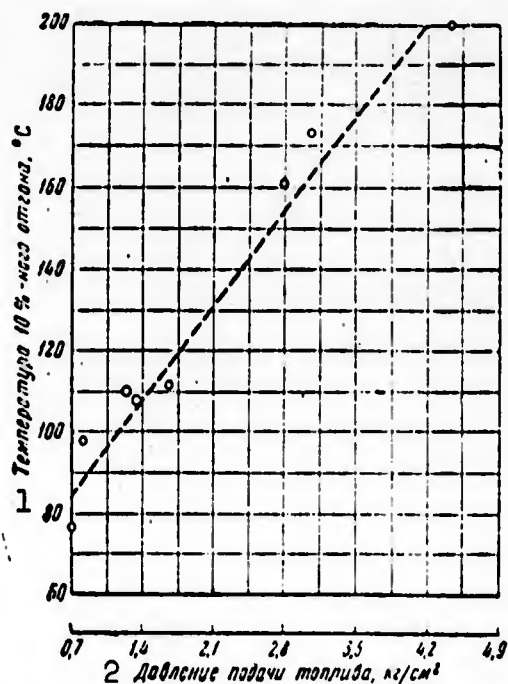
Fig. 111. Effect of the 10%-
distillation temperature on the
minimum vaporization pressure
at which starts are possible.
The mass flow rate of air is
0.227 kg/sec, and the air tem-
perature is 30°. 1) 10%-distil-
lation temperature, °C; 2) fuel-
feed pressure, kg/cm².

subsequently ignite suddenly during the starting period, resulting in
the overheating of the engine.

Figures 111 and 112 show the effect of the 10%-distillation tem-
perature of a fuel on the minimum pressure required for the vaporiza-
tion of the fuel, with the ignition of the fuel (from a standard source
such as an electric spark plug) still possible at this temperature. To
ignite a fuel having a 10%-distillation temperature of 80°, a pressure
of 0.7 kgf/cm² is adequate; at 200°, a pressure of 4.2 kgf/cm² is
needed. It is well known that the average dimension of a vaporized
fuel drop is approximately inversely proportional to the square of the
pressure at which vaporization takes place:

$$d_{cp} \sim \frac{1}{p^2}.$$

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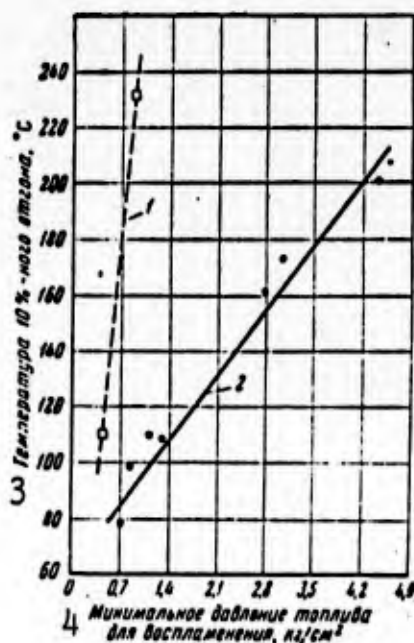
Fig. 112. Effect of 10%-distillation temperature on minimum vaporization pressure at which starts are possible. 1) High-power and low-pressure ignition system; 2) high-stress standard ignition system; 3) 10%-distillation temperature, ^{0}C; 4) minimum fuel pressure for ignition, kg/cm^2.

The higher the vaporization ratio, the easier the ignition of the fuel, since the vaporization surface increases, and the expenditures of energy and time on heating and vaporizing individual drops are reduced. Heavy fuels with low vapor tension require a greater vaporization ratio for ignition than do light fuels.

The effect of the 10%-distillation temperature on the starting characteristics of Soviet aviation fuel is presented in Fig. 113.

The best starting properties are exhibited by the B-70 gasoline, and the addition of this gasoline to the T-1 fuel will improve the starting properties.

In the case of heavy fuels, inadequate volatility may in part be compensated by a greater vaporization ratio. It is therefore not completely out of the question to use combustibles heavier than gasoline

for engine starting if structural changes can be introduced into the starter injectors and the ignition source, as well as by preliminary heating.
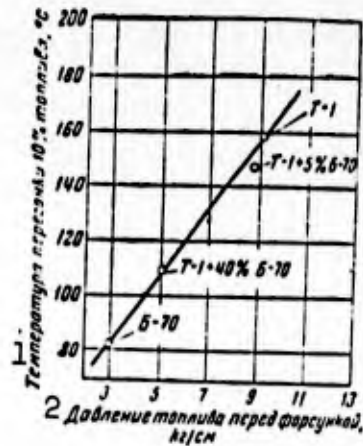
Fig. 113. Effect of 10%-distillation temperature on starting characteristics of fuels. 1) 10%-distillation temperature of fuel, $^{\circ}$C; 2) fuel pressure in front of injector (spray nozzle), kg/cm.

TABLE 81

Flash Point and Vapor Tension of Several Fuels [9, 18]

1 Топливо	2 Температура вспышки, °C	3 Упругость пара (мм рт.ст.) при температуре			
		20°	40°	60°	100°
T-1	+30	30	35	40	160
TC-1	+28	—	—	—	—
T-2	—12	60	100	150	475
T-5	+60	—	10	30	60
Дизельное топливо	11 От +50 до +125	—	—	—	..
Бензин Б-70	12 Ниже —28	—	200	—	—
н. Пентан	Ниже —40	—	—	—	—
н. Гексан	—22	—	—	—	—
н. Октан	+17	—	—	—	—
н. Декан	+46	—	—	—	—
Тетралин	+75	—	—	—	—

1) Fuel; 2) flash point, $^{\circ}$C; 3) vapor tension (mm Hg) at a temperature of; 4) diesel fuel; 5) B-70 gasoline; 6) n. pentane; 7) n. hexane; 8) n. octane; 9) n. decane; 10) tetralin; 11) from +50 to +125; 12) below —28.

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The flash point serves as the characteristic of ease of ignition or fuel flammability in case of contact with an open flame, i.e., the temperature of a combustible liquid at which the vapors of the combustible liquid above the liquid's surface ignite on contact with an open flame (Table 81).

Gasolines are characterized by a low flash point and high vapor tension; kerosenes are characterized by a higher flash point. However, it does not follow that the kerosenes do not ignite below the flash point under appropriate conditions.

Figure 114 shows the effect of fuel volatility on the ignition range (ignition accomplished by means of an electric spark plug) in the chamber of a turbojet engine at low pressures. A fuel of the JP-1 type (standard aviation kerosene which begins to boil at 160^{0}, of which 50% boils off below 213^{0}, and which ceases boiling at 280^{0}) has a narrower ignition range than a fuel of the JP-4 type of greater fractional composition (start of boiling, 53^{0}; 50% boils off below 185^{0}; end of boiling, 245^{0}).

For the ignition of air-reaction-engine fuels (TRD and PVRD [turbojet and ramjet engines]), the recommendations call for the injection of hypergolic substances into the combustion chamber, said substances to act as starter fuels. Triethylaluminum $Al(C_2H_5)_3$ and trimethylaluminum $Al(CH_3)_3$ are used for this purpose, and these substances are now made on an industrial scale [10]. It is also contended that borane fuels (such as B_5H_9) ignite and burn more easily than petroleum products; therefore, these can be used in jet aircraft at greater altitudes, where conventional fuels are incapable of combustion [11].

Trimethyl- and triethyl-aluminum have been tested by "Wright-Aeronautical" and "Curtis-Wright" for fuel ignition in a ramjet engine [12, 13]. Trimethylaluminum is used in a mixture with triethylaluminum,

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the latter having been added in order to reduce the freezing point of the trimethylaluminum. Trimethyl- and triethyl-aluminum are used also in combination with various jet fuels (in quantities of 15-20%) in order to provide for the rapid ignition of the jet fuels at great altitudes. Much work along these lines is being done in connection with ramjet, turbojet, and similar engines.
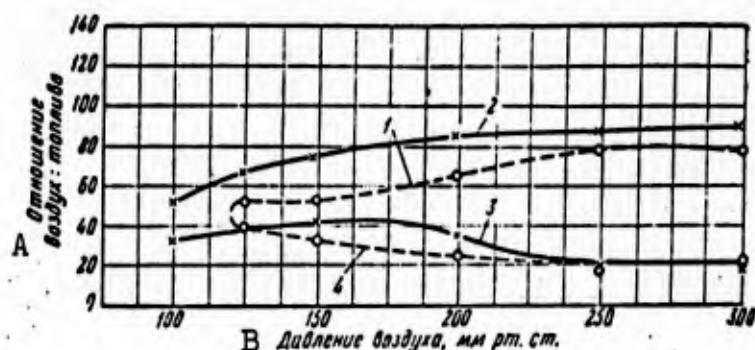
Fig. 114. Effect of fuel volatility on self-ignition range in the chamber of a turbojet engine at various pressures. 1 and 4) Lower and upper ignition limits for a fuel of the JP-1 kerosene type; 2 and 3) lower and upper limits of ignition for a fuel of wide fractional composition, such as a fuel of the JP-4 type. A) Air-to-fuel ratio; B) air pressure, mm Hg.

All of the above-enumerated compounds exhibit a small self-ignition lag in air, both in the case of atmospheric pressure, or in the case of reduced pressure.

The ignition lag for a number of elementary organic compounds under static conditions in air at 232°, and 127 mm Hg, is presented below:

Fuel	Self-ignition lag, sec
Trimethylaluminum $Al(CH_3)_3$.........	0.012
Triethylaluminum $Al(C_2H_5)_3$.........	0.040
Aluminum borohydride $Al(BH_4)_3$.....	0.010
Triethylboron $B(C_2H_5)_3$............	0.020
Tripropylboron $B(C_3H_7)_3$..........	0.210
Triisopropylboron $B(C_3H_7)_3$........	0.380

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Triethylphosphene $P(C_2H_5)_3$........   0.310
Kerosene.........................   210

The effect of pressure on the ignition lag in air at 232° is presented below:

Fuel	Pressure, mm Hg	Self-ignition lag, sec
Trimethylaluminum.......	30	0.003
	5	0.012
	2	0.020
	0.5	0.020
Triethylaluminum........	5	0.040
	2	0.080
. Triethylboron..........	5	0.020
	2	0.050
	0.5	0.040

With the addition of aviation kerosenes to the alkyl compounds of aluminum and boron, the self-ignition lag increases, and this can be seen from the following:

Fuel	Quantity of JP-5 in mixture, %	Ignition lag, sec
Trimethylaluminum..........	48	0.050
	61	0.450
	64.3	No ignition
Triethylboron.............	48	0.170
	60	0.200
	61.5	No ignition
Aluminum borohydride.......	83.6	0.010
	91.2	No ignition

The moisture of the air has a positive effect on ignition.

We can see from a brief review of the ignition properties of the metal alkyls that with a reduction in activity the latter can be placed into a series [14, 15]:

$$Al\,(BH_4)_3 > Al\,(CH_3)_3 > B\,(C_2H_5)_3 > Al\,(C_2H_5)_3.$$
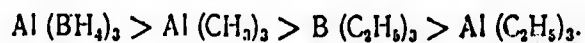
Ya.M. Paushkin and R.V. Sychev [16] in 1955 investigated the effect of triethylaluminum on the burning rate of a fuel in a jet engine. The addition of 1% triethylaluminum to a fuel consisting of aromatic

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hydrocarbons, increased the burning rate by a factor of two.

In 1960, Fletcher [17] and his coworkers published the results of an investigation into the burning of aluminum borohydride, trimethyl- and triethyl-aluminum, triethylboron, and pentaborane in the supersonic air stream produced by a ramjet engine. These investigations demonstrated that $Al(BH_4)_3$, B_5H_9, and their mixtures, containing up to 40% JP-4 aviation fuel, can burn stably at a supersonic airstream velocity of M = 2 (660 m/sec). The JP-4 fuel under these conditions can burn only if aluminum borohydride is injected. Trimethyl- and triethyl-boron does not ignite under the above-mentioned conditions in an operating chamber, but these can ignite on being exhausted from the nozzle of the engine [18].

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Chapter 8

RATE AND STABILITY OF JET-FUEL COMBUSTION

1. Rate of Combustion of Fuels

The process of fuel combustion in air-breathing jet engines takes place in a high-speed stream of air under the following conditions:

a) with the air passing through the engine at a considerably higher velocity than the normal velocity of flame propagation;

b) at air-to-fuel ratios outside the concentration range of ignition (in the secondary zone);

c) in variable operating modes of the engine in which the excess-air ratio reaches very high values.

Flame breakaway may take place at high air velocities when the engine's operating mode undergoes sharp variations. Combustion in which frequent flame breakaway may occur may be called unstable combustion.

The combustion process may be characterized by a normal propagation rate of the flame through the burning air-and-vapor mixture.

In normal burning of a mixture of vapors of a combustible substance with air, the flame front moves from layer to layer through the combustible mixture. A smooth and distinct flame front the velocity of which in the direction perpendicular to its surface is known as the normal combustion rate is formed in a laminar flow.

One method of determining the normal propagation rate of the flame consists in measuring the area S of the inner cone of a laminar Bunsen flame and the volume flow rate v of the combustible mixture.

The normal propagation rate of the flame is $u_n = v/S$. However, when fuel burns in air-breathing jet engines, we have the so-called turbulent combustion and agitation of the combustible mixture. The flame front is distorted, with the result that its surface area is increased, and the high-temperature combustion products are mixed with the air-and-vapor mixture, igniting it at various points.

In this case, the mass of burning substance per unit volume per unit time is much larger than in the case of normal laminar combustion. The flame-front turbulence and mixing of the unburned part of the fuel with the hot combustion products makes it possible to burn larger quantities of fuel in a short time.

The normal combustion rate cannot be used directly as, for example, for the design of an engine. But it does characterize the combustion processes of various combustible mixtures to a certain degree.

The normal combustion rates of individual hydrocarbons in mixture with air are listed in Table 82 as functions of their structure.

In saturated paraffinic hydrocarbons, the flame-propagation velocity increases slightly as the molecular weight increases (it is 33.8 cm/sec in methane and 40.2 cm/sec in decane).

The flame-propagation velocity in unsaturated hydrocarbons is higher than that in saturated hydrocarbons with the same number of carbon atoms (40.1 for ethane, 68.3 for ethylene, and 141 cm/sec for acetylene). In unsaturated hydrocarbons with a single double bond, the "degree of unsaturation" diminishes with increasing molecular weight, with the result that the combustion rate diminishes (68.3 for ethylene, 43.8 for butene-1, and 41.2 cm/sec for decene-1).

Naphthenes and aromatic hydrocarbons have virtually the same combustion rate as the paraffinic hydrocarbons, although the combustion rate of benzene is somewhat higher.

TABLE 82

Normal Flame-Propagation Rates in Combustion of Hydrocarbons in Air [1-6]

1 Углеводород	2 Формула	3 Максимальная скорость распространения пламени, см/сек
4 Парафины		
5 Метан	CH_4	33,8
6 Этан	C_2H_6	40,1
7 н. Пропан	C_3H_8	39,0
8 н. Бутан	C_4H_{10}	37,9
9 н. Пентан	C_5H_{12}	38,5
10 н. Гексан	C_6H_{14}	38,5
11 н. Гептан	C_7H_{16}	38,6
12 н. Декан	$C_{10}H_{22}$	40,2
13 н. Гексадекан	$C_{16}H_{34}$	40,7
14 2-Метилпропан	C_4H_{10}	34,9
15 2,2-Диметилпропан	C_5H_{12}	33,3
16 2-Метилбутан	C_5H_{12}	36,6
17 2,2-Диметилбутан	C_6H_{14}	36,7
18 2,3-Диметилбутан	C_6H_{14}	35,9
19 2-Метилпентан	C_6H_{14}	36,8
20 3-Метилпентан	C_6H_{14}	36,7
21 2,2-Диметилпентан	C_7H_{16}	34,8
22 2,3-Диметилпентан	C_7H_{16}	36,5
23 2,4-Диметилпентан	C_7H_{16}	35,7
24 3,3-Диметилпентан	C_7H_{16}	35,3
25 2,2,4-Триметилпентан	C_8H_{18}	34,6
26 Олефины		
27 Этен	C_2H_4	68,3
28 Пропен	C_3H_6	43,8
29 Бутен-1	C_4H_8	43,2
30 Пентен-1	C_5H_{10}	42,6
31 Гексен-1	C_6H_{12}	42,1
32 Децен-1	$C_{10}H_{20}$	41,2
33 2-Метилпропен-1	C_4H_8	37,5
34 2-Метилбутен-1	C_5H_{10}	39,0
35 3-Метилбутен-1	C_5H_{10}	41,5
36 2-Этилбутен-1	C_6H_{12}	39,3
37 2-Метилпентен-1	C_6H_{12}	39,6
38 4-Метилпентен-1	C_6H_{12}	40,5
39 Диолефины		
40 Бутадиен-1,2	C_4H_6	58,0
41 Бутадиен-1,3	C_4H_6	54,5
42 цис-Пентадиен-1,3	C_5H_8	46,5
43 транс-Пентадиен-1,3	C_5H_8	45,6
44 Пентадиен-1,2	C_5H_8	51,8
45 Пентадиен-2,3	C_5H_8	50,7
46 Пентадиен-1,4	C_5H_8	46,6
47 Гексадиен-1,5	C_6H_{10}	44,2
48 2-Метилбутадиен-1,3	C_5H_{10}	45,0
49 2,3-Диметилбутадиен-1,3	C_6H_8	41,6

TABLE 82 (Conclusion)

1 Углеводород	2 Формула	3 Максимальная скорость распространения пламени, см/сек
50 Ацетиленовые углеводороды		
51 Этин	C_2H_2	141,0
52 Пропин	C_3H_4	69,9
53 Бутин-1	C_4H_6	58,1
54 Пентин-1	C_5H_8	52,9
55 Гексин-1	C_6H_{10}	48,5
56 Бутин-2	C_4H_6	51,5
57 Гексин-3	C_6H_{10}	45,4
58 3,3-Диметилбутин-1	C_6H_{10}	47,7
59 4-Метилпентин-1	C_6H_{10}	45,0
60 4-Метилпентин-2	C_6H_{10}	45,8
61 Циклопарафины		
62 Циклопропан	C_3H_6	49,5
63 Циклопентан	C_5H_{10}	37,7
64 Циклогексан	C_6H_{12}	38,7
65 Метилциклопентан	C_6H_{12}	36,0
66 Метилциклогексан	C_7H_{14}	37,5
67 транс-Декалин	$C_{10}H_{18}$	36,2
68 Ароматические углеводороды		
69 Бензол	C_6H_6	44,6
70 Толуол	C_7H_8	38,8
71 о-Ксилол	C_8H_{10}	34,4
72 н. Бутилбензол	$C_{10}H_{14}$	35,9
73 трет. Бутилбензол	$C_{10}H_{14}$	36,6
74 Тетралин	$C_{10}H_{12}$	36,5

1) Hydrocarbon; 2) formula; 3) maximum propagation velocity of flame, cm/sec; 4) paraffins; 5) methane; 6) ethane; 7) n-propane; 8) n-butane; 9) n-pentane; 10) n-hexane; 11) n-heptane; 12) n-decane; 13) n-hexadecane; 14) 2-methylpropane; 15) 2,2-dimethylpropane; 16) 2-methylbutane; 17) 2,2-dimethylbutane; 18) 2,3-dimethylbutane; 19) 2-methylpentane; 20) 3-methylpentane; 21) 2,2-dimethylpentane; 22) 2,3-dimethylpentane; 23) 2,4-dimethylpentane; 24) 3,3-dimethylpentane; 25) 2,2,4-trimethylpentane; 26) olefins; 27) ethene; 28) propene; 29) butene-1; 30) pentene-1; 31) hexene-1; 32) decene-1; 33) 2-methylpropene-1; 34) 2-methylbutene-1; 35) 3-methylbutene-1; 36) 2-ethylbutene-1; 37) 2-methylpentene-1; 38) 4-methylpentene-1; 39) diolefins; 40) butadiene-1,2; 41) butadiene-1,3; 42) cis-pentadiene-1,3; 43) trans-pentadiene-1,3; 44) pentadiene-1,2; 45) pentadiene-2,3; 46) pentadiene-1,4; 47) hexadiene-1,5; 48) 2-methylbutadiene-1,3; 49) 2,3-dimethylbutadiene-1,3; 50) acetylenic hydrocarbons; 51) ethyne; 52) propyne; 53) butyne-1; 54) pentyne-1; 55) hexyne-1; 56) butyne-2; 57) hexyne-3; 58) 3,3-dimethylbutyne-1; 59) 4-methylpentyne-1; 60) 4-methylpentyne-2; 61) cycloparaffins; 62) cyclopropane; 63) cyclopentane; 64) cyclohexane; 65) methylcyclopentane; 66) methylcyclohexane; 67) trans-decalin; 68) aromatic hydrocarbons; 69) benzene; 70) toluene; 71) o-xylene; 72) n-butylbenzene; 73) tert-butylbenzene; 74) tetralin.

The maximum flame-propagation velocities in hydrocarbons of various structures are shown in Figs. 115-118.

The flame-propagation velocity is a function of the fuel-to-air ratio. The highest flame velocity is reached in the majority of fuels in rich mixtures 10 to 30% above the stoichiometric ratio. Benzene, for which the maximum flame-propagation rate is reached at 60% excess fuel, constitutes an exception.

The propagation velocity of the flame depends on the pressure at which the combustion process takes place (Fig. 114). When the pressure is reduced below atmospheric, the combustion rate first increases and then diminishes [7].
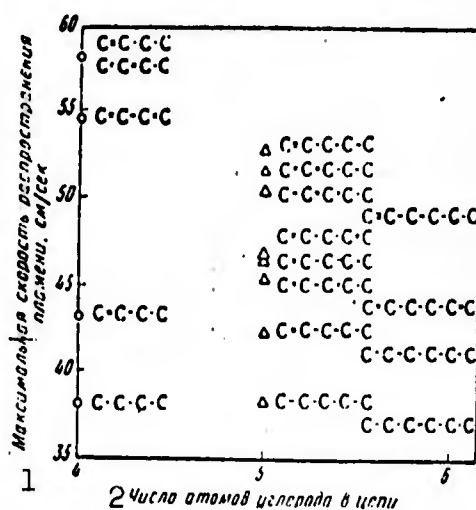
Fig. 115. Influence of hydrocarbon structure and molecular weight on maximum velocity of flame propagation in hydrocarbons mixed with air. 1) Maximum flame-propagation velocity, cm/sec; 2) number of carbon atoms in chain.

The normal velocity of flame propagation also depends on the temperature of the vapor-air mixture through which the flame is propagating (Fig. 119). It increases approximately linearly with increasing temperature. Thus, the normal rate of flame propagation in heptane

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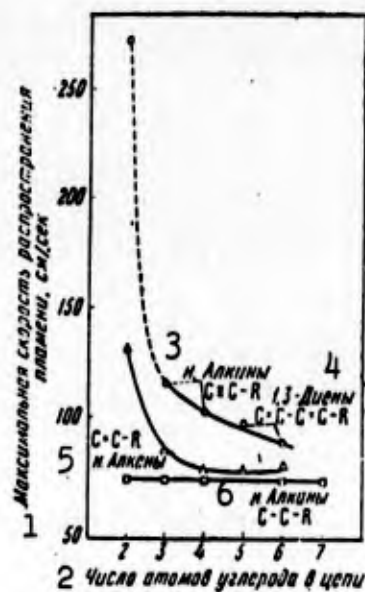
Fig. 116. Influence of hydro-
carbon structure and molecular
weight on maximum propagation
velocity of flame in hydrocar-
bons mixed with air. 1) Maximum
flame-propagation velocity,
cm/sec; 2) number of carbon
atoms in chain; 3) normal al-
kynes; 4) 1,3-dienes; 5) normal
alkenes; 6) normal alkanes.
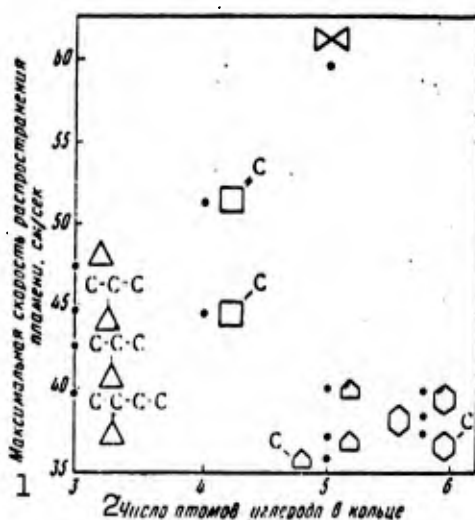
Fig. 117. Influence of hydro-
carbon structure and molecular
weight on maximum rate of
flame propagation in hydrocar-
bons mixed with air. 1) Maximum
flame-propagation velocity,
cm/sec; 2) number of carbon
atoms in ring.

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Fig. 118. Influence of hydro-
carbon structure and molecular
weight on maximum velocity of
flame propagation in hydrocar-
bons mixed with air. 1) Maximum
flame-propagation rate, cm/sec;
2) number of carbon atoms in
chain; 3) alkenes; 4) alkynes;
5) alkenes; 6) alkanes; 7) cy-
cloalkanes.
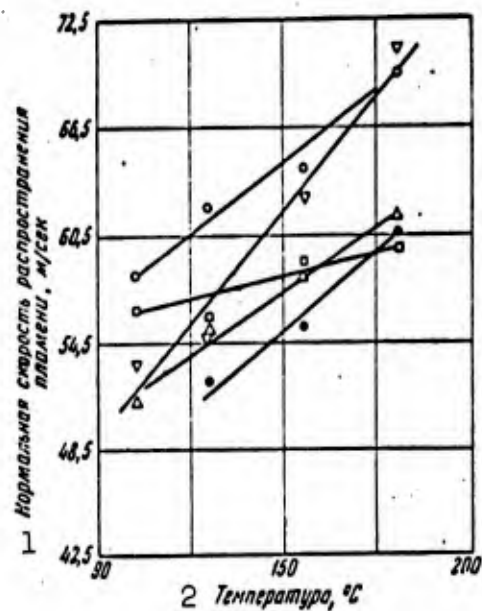
Fig. 119. Influence of tempera-
ture of vapor-air mixture on
normal flame-propagation veloc-
ity. ∇) $n-C_6H_{14}$; ○) C_7H_{16}; Δ)
$C_6H_5CH_3$; ●) $n-C_8H_{18}$; □) $n-C_8H_{16}$;
1) normal flame-propagation
velocity, m/sec; 2) tempera-
ture, °C.

mixed with air depends on temperature in the following manner [6]:

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Temperature, ^{o}C	Rate of flame propagation, cm/sec
20	38.6
100	56
150	64
200	72

It is interesting to examine the rates of combustion of hydrocarbon derivatives (Table 83).

As will be seen from the data presented here, hydrocarbon derivatives have higher combustion rates in many cases than do the hydrocarbons themselves.

Table 84 lists the combustion rates of gasoline with tetranitromethane additives.

Tetranitromethane has little effect on the combustion rate. However, the influence of additives on combustion rate is not in general adequately understood as yet, although they are known to be helpful in self-ignition processes.

Hydrocarbons burning at high rates have higher combustion temperatures. Below we list combustion rates of hydrocarbons in air and the theoretical equilibrium temperatures of combustion (Table 85).

In the majority of cases, the rate and temperature of combustion vary in the same direction.

The temperature to which the matter is heated on combustion of a mixture varies from layer to layer [8-10].

This problem has been illuminated by Ya.B. Zel'dovich and K.S. Zarembo [8] for the Bunsen flame; these investigators showed that heating of the unburned mixture occupies a region of about 1.5 mm. The possibility is not excluded that it is precisely in this region that pre-ignition reactions take place, particularly for fuels with large complex-structured molecules, which are particularly sensitive to thermal and oxidative disturbances. At the same time, such transformations may

TABLE 83

Rate of Flame Propagation in Hydrocarbon Derivatives Mixed with Air [1, 2]

1 Вещество	2 Максимальная скорость распространения пламени, см/сек
3 Окись этилена	89,5
4 Окись пропилена	67,2
5 Метанол	57,2
6 Этанол	55,6
7 Изопропанол	41,5
8 Диэтиловый эфир	49,8
9 Изопропиловый эфир	49,7
10 Нитроэтан	47,6
11 Нитропропан	48,3

1) Substance; 2) maximum flame-propagation rate, cm/sec; 3) ethylene oxide; 4) propylene oxide; 5) methanol; 6) ethanol; 7) isopropanol; 8) diethyl ether; 9) isopropyl ether; 10) nitroethane; 11) nitropropane.

TABLE 84

Combustion Rates of Gasoline Vapor with Air and Tetranitromethane Additive [1, 2]

1 Топливо	2 Добавка $C(NO_2)_4$, %	3 Скорость горения, см/сек
4 Легкий бензин . . .	5 Нет	48,5
» »	5	49,0
» »	10	53,4
» »	15	54,0

1) Fuel; 2) $C(NO_2)_4$ additive, %; 3) combustion rate, cm/sec; 4) light-fraction gasoline; 5) none.

not even occur in the low-temperature zone for fuels with simple molecules (hydrogen, carbon monoxide, methane).

The rate of flame propagation apparently depends on the induction period, during which the combustible mixture is heated to the ignition point by the hot products of combustion. Thus, it has been shown ex-

TABLE 85

Rate of Flame Propagation in Hydro-
carbon-and-Air Mixtures and Their
Combustion Temperatures [5]

1 Углеводород	Температура 2 горения, °C	Скорость рас-пространения пламени, см/сек 3
4 Ацетилен	2322	157.
5 Этилен	2112	74
6 Бензол	2102	47,8
7 Циклогексан	2027	43,6
8 Гептан	2007	42,4
9 Пропан	1967	45,5
10 Бензин	2102	47,8

1) Hydrocarbon; 2) combustion tem-
perature, °C; 3) velocity of flame
propagation, cm/sec; 4) acetylene;
5) ethylene; 6) benzene; 7) cyclohex-
ane; 8) heptane; 9) propane; 10) gas-
oline.
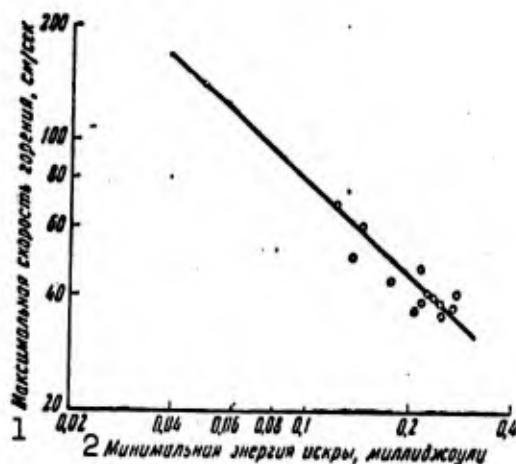
Fig. 120. Flame-propagation
rate as a function of minimum
ignition energy. 1) Maximum
combustion rate, cm/sec; 2)
minimal sparking energy, milli-
joules.

perimentally that the rate of flame propagation is inversely propor-

tional to the minimum energy of the electric spark required to ignite

the combustible mixture (Fig. 120).

The normal velocity of flame propagation can be computed theoreti-

cally. According to the combustion theory of N.N. Semenov and Ya.B.

Zel'dovich [11-13], the normal combustion rate is determined by the equation

$$u_{\text{n}} = \sqrt{\frac{2\lambda \cdot A \cdot e^{-\frac{E}{RT}} \cdot RT^2}{C_p \cdot \rho_0 \cdot a\,(T - T_0)\,E}} \; ,$$

where u_{n} is the linear velocity of flame propagation, λ is the coefficient of thermal conductivity, A is a constant, E is the activation energy, R is the gas constant, T is the adiabatic equilibrium temperature of the flame, C_p is the specific heat capacity at constant pressure, $\underline{a}$ is the initial concentration of the reagents, ρ_0 is the density, α is the heat-transfer coefficient and T_0 is the initial temperature.

In a number of cases, the experimental and computed flame-propagation velocities agree quite well. Thus, the experimental values for propane and ethylene are 39 and 68 cm/sec, while those computed by the above formula are, respectively, 38.3 and 71.0 cm/sec.

The smaller the activation energy, the higher will be the rate of normal flame propagation:

Hydrocarbon	cal/mole	cm/sec
Acetylene.............	20,000	144.0
Ethane...............	26,000	40.1
Ethylene.............	24,000	68.2
Isopentane...........	27,000	36.6

In propagation of a flame in a quiet medium and in laminar flow of the combustible mixture, a smooth and distinct flame front is formed. In turbulent flow, the flame front loses its definition and becomes uneven under the influence of pulsation. For this reason, the area of a turbulent-flame front is larger than that of a laminar-flame front. The movement of the flame front in turbulent combustion in the direction perpendicular to its surface is known as the turbulent rate of

propagation of the flame [14]. It depends on the physicochemical prop-
erties of the combustible mixture and the aerodynamic conditions,
which are characterized by the Reynolds number Re:

$$u_t = u_{\text{н}} \sqrt{1 + k\,\text{Re}};$$
$$u_t = u_{\text{н}} \sqrt{1 + \frac{\varepsilon}{a}}.$$

where $\underline{k}$ is a coefficient, ε is the turbulent-diffusion coefficient,
and $\underline{a}$ is the molecular coefficient of thermal conductivity.
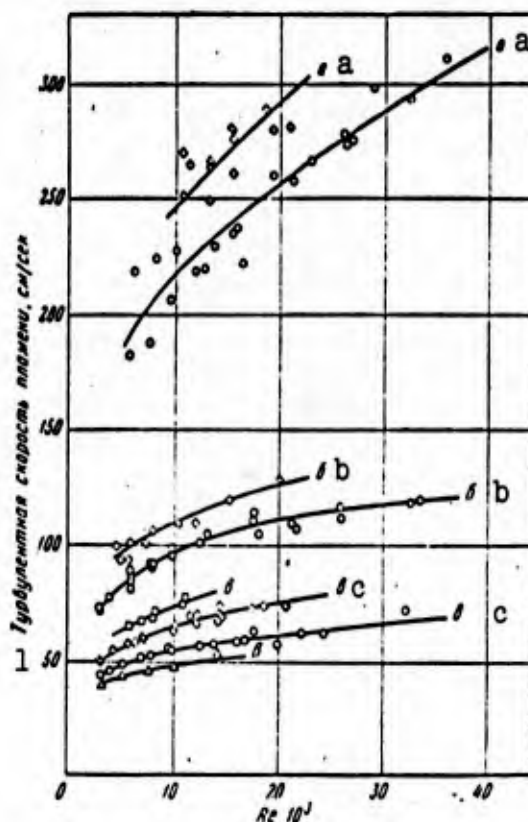
Fig. 121. Combustion rate of fuels as
a function of Reynolds number. a)
Acetylene ($u_n = 147$ cm/sec); b) ethyl-
ene ($u_n = 70$ cm/sec); c) propane
($u_n = 45$ cm/sec). 1) Turbulent veloc-
ity of flame, cm/sec.

The variation of flame-propagation rate as a function of Reynolds
number is shown in Fig. 121.

The combustion rate may be almost doubled in the experiments un-
der consideration due to "turbulization."

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When a liquid fuel is burned in a combustion chamber, nozzles that atomize the fuel into fine droplets are used for fuel feed. The burning of the flame as a whole is the sum of the combustion of the individual droplets forming it. Analysis of the physical pattern of the combustion process for the individual drop makes it possible to pass to a characterization of the process as a whole.

L.N. Khitrin [15] presents the burning time of a droplet in the following form as a function of its initial radius r_0 and other factors:

$$\tau = \frac{\gamma_{\text{\tiny ж}} \cdot \frac{L}{\lambda}}{2(T_c - T_{\text{\tiny к}})} \cdot r_0^2,$$

where γ_{zh} is the density of the fuel at the boiling point, L is the latent heat of evaporation, λ is the coefficient of thermal conductivity of the gaseous medium, T_s is the ambient temperature (the combustion temperature of the fuel in the chamber), T_k is the boiling point of the fuel and τ is the burning time. This equation is valid for the most simple cases; it implies that the combustion time for a droplet is directly proportional to the square of the droplet's initial radius.

G.N. Khudyakov [16] studied the process in which liquids burn from a free horizontal surface, as well as the combustion of liquid-fuel droplets in flight. The combustion of a liquid from a free surface may be regarded as the first stage in a comparative characterization of the combustion of liquids. The combustion process of a liquid fuel is composed of its heating, vaporization, mixture of the vapors with an oxidizer (air), ignition of the resulting mixture, and combustion of the vapor-and-air mixture.

The combustion process is composed of the times spent in the following individual stages:

1) heating and vaporization of the droplet;

TABLE 86

Rate of Combustion of Liquid Fuels from Free Surface and Normal Combustion Rate [16]

1 Горючее	2 T. кип., °C	3 Плотность при 20°	4 Скорость играния жидкостей, мм/мин	5 Нормальная скорость распространения пламени, см/сек
6 Петролейный эфир	—	0,710	2,45	—
7 Авиационный бензин	50—170	0,730	2,10	44,6
8 Автомобильный бензин	60—220	0,770	1,75	—
9 Керосин	150—300	0,840	0,97	36
10 Бензол	80	0,875	3,15	44,8
11 Толуол	110	0,860	2,68	38,8
12 Метиловый спирт	—	0,800	1,20	57
13 Зеленое масло пиролиза	—	0,928	1,30	—
14 Машинное масло	—	0,900	0,74	—

1) Fuel; 2) b.p., °C; 3) density at 20°; 4) rate of combustion of liquids, mm/min; 5) normal rate of flame propagation, cm/sec; 6) petroleum ether; 7) aviation gasoline; 8) automobile gasoline; 9) kerosene; 10) benzene; 11) toluene; 12) methyl alcohol; 13) green pyrolysis oil; 14) machine oil.

2) mixing of the resulting combustible vapors with the oxidant;

3) the ignition delay;

4) the time for propagation of the flame through the air-and-vapor mixture.

The slowest process is the first stage, the rate of which depends on the size of the droplet, which determines the rate at which the latter is heated up.

Since evaporation of a combustible liquid takes place at the expense of the radiant heat of a flame, a certain heat-transfer relationship is established in the steady-state process:

$$\left. \begin{array}{r} \text{heat expended on} \\ \text{evaporation of liquid} \end{array} \right\} = \left\{ \begin{array}{l} \text{heat flow to} \\ \text{surface of liquid} \end{array} \right.$$

$$v\gamma \left[i + c \left(t_к - t_ж \right) \right] = \alpha \left(t_{гор} - t_к \right)$$

$$v = \frac{\alpha \left(t_{гор} - t_к \right)}{\gamma \left[i + c \left(t_к - t_ж \right) \right]},$$

where $\underline{v}$ is the combustion rate, γ is the density, $\underline{i}$ is the latent heat

of evaporation, t_k is the boiling point and the surface temperature of the boiling liquid, t_{zh} is the initial temperature of the liquid, $\alpha(t_{gor} - t_k)$ is the heat flow to the liquid surface, t_{gor} is the combustion temperature and α is the heat-transfer coefficient.

The above equation is a heat-balance equation; in elementary form, it characterizes the factors on which the liquid's combustion rate depends from the standpoint of heat transfer. However, this relationship assumes a more complex form for combustion of a droplet.

Table 86 presents the surface combustion rates of a series of liquids according to the data of G.N. Khudyakov [16].

The combustion rate may be used for comparative characterization of individual fuels. It follows from this that the volatility of liquid fuels is a decisive factor in their combustion, while the normal flame-propagation rate is of the same order for the majority of fuels.

2. Stability of Fuel Combustion

By the term "stability of combustion" we imply the property of maintaining a flame front through various deviations from the normal mode toward either leaner or richer mixtures.

TABLE 87

Influence of Air Pressure and Temperature on Range of Stable Combustion for Gasoline [18]

1 Давление, am	2 Скорость воздуха, м/сек	3 Температура воздуха, °C	Пределы стабильного горения, отношение к стехнометрическому составу 4
0,2	140	150	1,31—0,69
1,1	120	150	1,08—0,60
1	83	96	1,27—0,77
1	83	165	1,37—0,76
1	83	204	1,37—0,73
1	83	260	1,37—0,69

1) Pressure, atm; 2) air velocity, m/sec; 3) air temperature, °C; 4) range of stable combustion; ratio to stoichiometric composition.
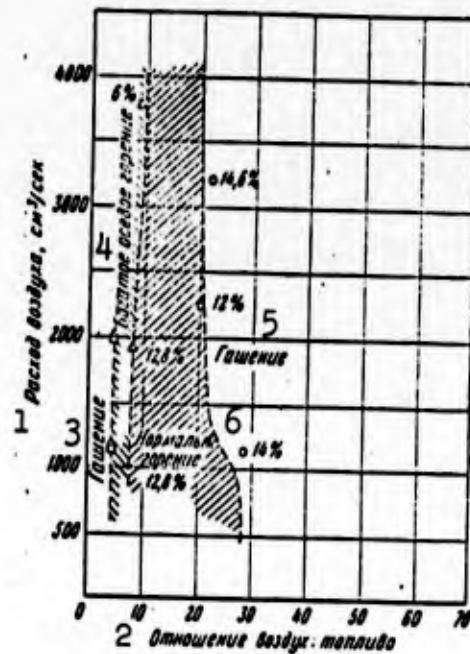
Fig. 122. Range of stable combustion for isooctane. 1) Air consumption, cm^3/sec; 2) air-to-fuel ratio; 3) extinction; 4) rich-mixture axial combustion; 5) extinction; 6) normal combustion.

The normal stable operating mode of the engine corresponds to air-to-fuel ratios ranging from 5:1 to 120:1. In cases of acceleration or deceleration, these limits may be extended to 20:1 to 600:1.

The influence of the fuel's chemical composition on its range of stable combustion has been studied in various experimental apparatus and chambers.

Figures 122 and 123 show the limits of stable combustion for isooctane and toluene [17].

The data shown were obtained in an investigation carried out with a chamber formed by a quartz tube 600 mm long and 25 mm in diameter. A special burner into which the fuel vapor and air were fed was set up at one end of the tube. Combustion stability was characterized by the maximum flow rate of the working mixture (cm^3/sec), at which flame breakaway was observed. The air-to-fuel ratio was held constant in the
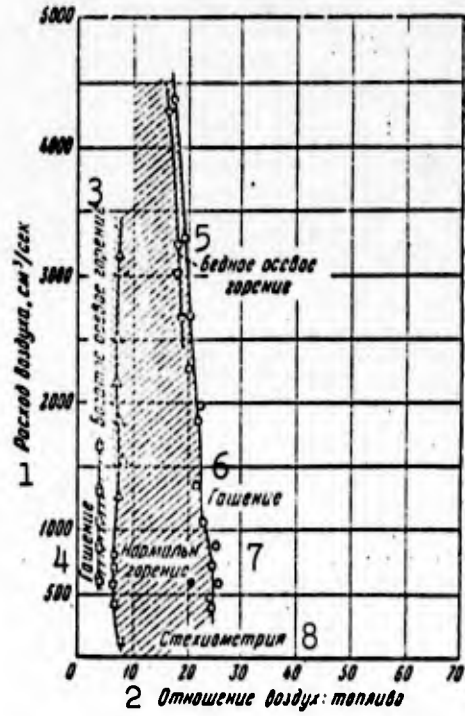
Fig. 123. Stable-combustion
range for toluene. 1) Air con-
sumption, cm^3/sec; 2) air-to-
fuel ratio; 3) rich-mixture
axial combustion; 4) extinc-
tion; 5) lean-mixture axial
combustion; 6) extinction; 7)
normal combustion; 8) stoichi-
ometry.
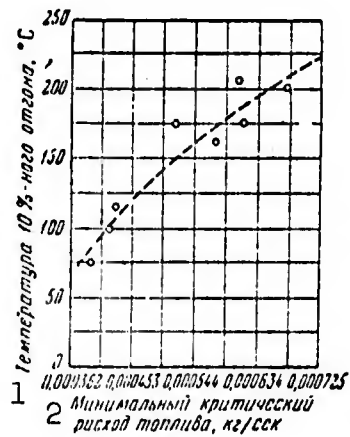
Fig. 124. Minimum critical fuel
consumption as a function of
temperature of 10% distillation
of fuel. 1) Temperature of 10%
distillation, ^{O}C; 2) minimum
critical fuel consumption,
kg/sec.

process.

Acetylene has a broad range of stable combustion in mixtures with air. The other hydrocarbons (paraffins, naphthenes, aromatic hydrocarbons) have closely similar stable-combustion ranges.

It will apparently be impossible to achieve any essential broadening of the stable-combustion range by manipulating the chemical composition of the fuel, since such substances as acetylene and its homologs can hardly be used in practice. Adequate study has not as yet been devoted to the significance of various fuel additives in expanding the stable-combustion range.

The range of stable combustion depends on the combustion conditions of the fuel. Table 87 shows the range of stable combustion for gasoline in an experimental chamber as a function of the pressure and temperature of the air fed to it.

The critical fuel-flow rate, at which flame breakaway may be observed, depends on the volatility of the fuel, which is characterized by the temperature of 10% distillation. Thus, flame breakaway is reached in the combustion of gasoline at leaner mixtures than in the combustion of kerosene. Kerosene is superior to gas oil in this respect [18]. This situation is illustrated by Fig. 124.

When gas oils with boiling ranges from 240 to 365 and 207 to 400° are used as fuels, it is impossible to start the engine. After the engine has been started on a light fuel, however, it can continue running. Neither starting nor running was possible in the case of gas oils with the boiling range 260 to 396°.

Apart from volatility, the combustion stability of a fuel depends on the degree to which it is atomized and the quality of mixture formation. The quality of atomization depends in turn on the viscosity and surface tension of the fuel. It is considered that with fuel viscosities

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higher than 15 centistokes, atomization quality may deteriorate considerably. At normal temperatures, the viscosities of jet fuels run to 2-3 centistokes, but at low temperatures they may increase considerably. Negative viscosity values can be reduced by heating the fuel [18]. Contemporary conceptions of fuel combustion are set forth in References [19, 20].

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[List of Transliterated Symbols]

317   н = n = normal'nyy = normal

319   ж = zh = zhidkost' = liquid

319   c = s = sreda = medium

319   к = k = kipeniye = boiling

320   гор = gor = goreniye = combustion

Part Two

FUELS FOR LIQUID REACTION ENGINES

Chapter 1

GENERAL INFORMATION ON ENERGY SOURCES AND FUELS
FOR LIQUID REACTION ENGINES

1. Characteristics of Energy Sources for Liquid Reaction Engines

Systems consisting of one or several substances capable of burning at high speed in an engine chamber and liberating large quantities of heat and gases can be considered to be energy sources (fuels). The term conversion encompasses not only combustion but any chemical process accompanied by the liberation of energy.

In practice, reactions in which various elements are oxidized, chiefly by oxygen and fluorine, are associated with the concept of combustion. The essence of oxidation lies in the transfer of electrons from the substance being oxidized to an atom of the oxidizer.

We must keep in mind, however, that a large amount of energy can be liberated not only in oxidation reactions such as, for example, the oxidation of carbon by oxygen:

$$C + O_2 \rightarrow CO_2 + 94.05 \text{ kcal/mole, or } 2150 \text{ kcal/kg,}$$
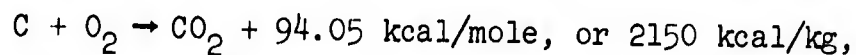
but also in reduction reactions, for example the reduction of carbon monoxide by hydrogen:

$$CO + 3H_2 \rightarrow CH_4 + H_2O + 46 \text{ kcal/mole, or } 1440 \text{ kcal/kg,}$$
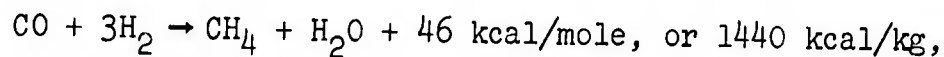
as well as in reactions in which hydrogen may be considered to be an oxidizer as, for example, in the formation of lithium hydride:

$$Li + 1/2H_2 \rightarrow LiH + 21.6 \text{ kcal/mole, or } 2730 \text{ kcal/kg.}$$
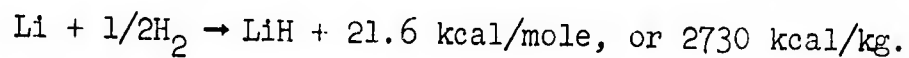
For the sake of comparison, let us note that a solid propellant

liberates 800-1200 kcal/kg upon combustion.

Reactions accompanied by the liberation of heat and light are observed in systems in which oxidation or reduction does not occur in the normal sense, i.e., in the dissociation of ozone:

$$O_3 \rightarrow 1\text{-}1/2 O_2 + 34 \text{ kcal/mole, or } 708 \text{ kcal/kg.}$$
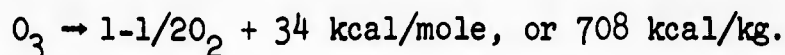
A process superficially resembling combustion will be observed upon recombination of atoms into molecules, for example:

$$0 + 0 \rightarrow O_2 + 116.4 \text{ kcal/mole, or } 3640 \text{ kcal/kg.}$$
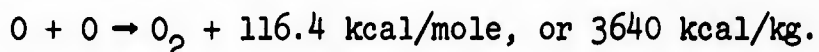
Thus, the number of processes in which a large amount of energy is developed is not limited solely to combustion or oxidation processes.

In practice, however, it is chiefly the energy of oxidation processes that is used in engines.

a) The energy of oxidizing processes

The liberation of heat during oxidizing processes is the most common method of obtaining energy. Processes accompanied by the liberation of more than 1000-1200 kcal/kg are chiefly used in ZhRD.

The energy efficiency of combustion processes is characterized by the heat of reaction and by the amount of heat liberated per unit weight of fuel.

The fuel may take the form of a combination of several substances (oxidizer and combustible) or may consist of a single substance. The heat of reaction per unit weight of fuel (combustible + oxidizer) is called the heat yield to distinguish it from heating value, which is employed to characterize fuels burning at the expense of the oxygen of the air.

To illustrate oxidation reactions, we give the following oxidizing processes (Table 88).

The three last oxidation reactions shown in Table 88 are charac-

TABLE 88

Heat of Reaction Characteristics for Oxidizing Processes [1-3]

1 Реакция	2 Тепловой эффект, ккал		
	3 на з-моль	4 на 1 кг горючего	5 на 1 кг смеси горючего и окислителя
$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$ . . .	57,8 *	28900	3218
$C + O_2 \rightarrow CO_2$	94,05	7860	2145
$2Al + 1\tfrac{1}{2}O_2 \rightarrow Al_2O_3$ . . .	402	7380	3940
$2P + 2\tfrac{1}{2}O_2 \rightarrow P_2O_5$ . . .	360	5810	2558
$Si + 2F_2 \rightarrow SiF_4$ . . .	373,0	—	3460
$Al + 1\tfrac{1}{2}F_2 \rightarrow AlF_3$ . . .	329	—	3940
$B + 1\tfrac{1}{2}F_2 \rightarrow BF_3$ . . .	267,0	—	3805
$\tfrac{1}{2}H_2 + \tfrac{1}{2}F_2 \rightarrow HF$ . . .	64,2*	—	3219
$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 \rightarrow HCl$ . . .	21,89	—	603

*Without allowing for the heat of condensation.

1) Reaction; 2) heat of reaction, kcal; 3) per g-mole; 4) per kg of combustible; 5) per kg of combustible-oxidizer mixture.

terized by low reaction heat and, naturally, cannot be used as energy sources.

In many cases, substances may be used as fuels that contain free oxygen (for example, bound by nitrogen) capable of combining with other elements upon breakdown of the substance, with the liberation of large amounts of heat.

Examples of such substances are nitroglycerine and nitromethane:

$$4C_3H_5(ONO_2)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2 + 1485 \text{ kcal/kg}$$
$$CH_3NO_2 \rightarrow CO + H_2O + \tfrac{1}{2}H_2 + \tfrac{1}{2}N_2 + 1030 \text{ kcal/kg}.$$
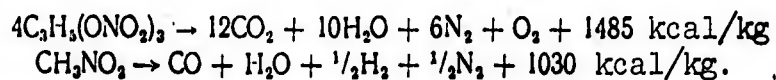
Substances that decompose and liberate a large amount of energy are explosive to some degree or other. Their use in liquid reaction engines in certain cases is confined to experimental investigations, and in other cases is limited to the use of substances having low heats of decomposition.

b) Breakdown energy of endothermic substances

Certain substances whose formation is accompanied by the absorp-

tion of energy liberate this energy when they decompose. In principle, reactions in which endothermic substances break down into elements or groups of atoms may be considered as energy sources.

Thus, 54.9 kcal of heat is absorbed upon the formation of a gram-molecule of acetylene from hydrogen and oxygen. Upon decomposition of the acetylene, this energy is liberated completely:

$$HC \equiv CH \rightarrow 2C + H_2 + 54.9 \text{ kcal/mole (2110 kcal/kg)}.$$
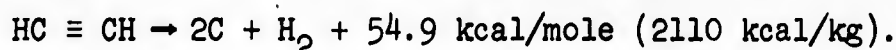
The liquid polymer of acetylene (divinylacetylene) decomposes similarly:

$$CH_2 = CH - C \equiv C - CH = CH_2 \nearrow^{6C + 3H_2 + 76 \text{ kcal/mole (980 kcal/kg)}}_{\searrow 1\frac{1}{2}CH_4 + 4\frac{1}{2}C + 1250 \text{ kcal/kg}.}$$
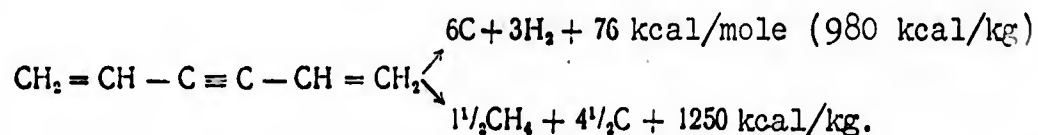
These reactions find no technical application, since the explosive properties of acetylene prevent its application in technology in the liquid or compressed form. In oxygen-acetylene welding, however, the energy of the endothermic breakdown of acetylene is used; it is added to the energy of oxidation:

$$C_2H_2 + 2,5O_2 \rightarrow 2CO_2 + H_2O + 2770 \text{ kcal/kg}.$$
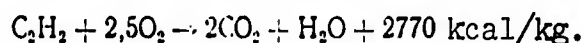
The explosive breakdown reactions of such endothermic compounds as lead azide and mercury fulminate find application in technology:

$$PbN_6 \rightarrow Pb + 3N_2 + 367 \text{ kcal/kg}$$
$$Hg(CNO)_2 \rightarrow Hg + 2C + N_2 + O_2 + 414 \text{ kcal/kg}.$$
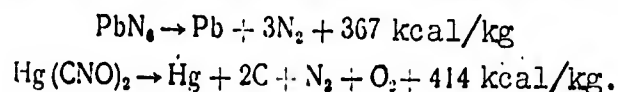
These reactions are used as detonators for explosives.

Table 89 gives the decomposition energy for several endothermic compounds.

Among the endothermic compounds, acetylene and hydrazoic acid possess the greatest energies of decomposition.

These compounds cannot be used in rocket engines, at least at the present time, owing to their explosiveness.

A breakdown reaction of endothermic compounds may be accompanied

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by the formation of complex molecules with the liberation of an additional amount of heat as, for example, in the case of hydrazine:

$$N_2H_4 \rightarrow 1\frac{1}{3}NH_3 + \frac{2}{3}N_2 + 26.3 \text{ kcal/mole, or } 825 \text{ kcal/kg.}$$
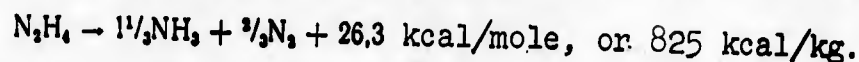
Hydrazine is a substance that presents considerable interest for rocket engineering.

TABLE 89

Heating Value of Breakdown Reactions of Endothermic Compounds [4]

1 Соединение	2 Формула	3 Мол. вес	4 Теплота образования, ккал/моль	5 Теплопроизводительность, ккал/кг
6 Ацетилен	C_2H_2	26	−54,9	2110
7 Азотистоводородная кислота	HN_3	43	−61,0	1420
8 Дициан	C_2N_2	52	−65,5	1260
9 Синильная кислота	HCN	27	−23,6	875
10 Закись азота	N_2O	44	−19,5	447
11 Окись азота	NO	30	−21,6	720
12 Озон	O_3	48	−34	708
13 Азид кальция	$Ca(N_3)_2$	124,1	−75,7	610
14 Азид меди	CuN_3	105	−56,9	540
15 Треххлористый азот	NCl_3	120,4	−54,7	454
16 Двуокись хлора	ClO_2	67,5	−30,1	446
17 Азид свинца	$Pb(N_3)_2$	—	−103,0	367
18 Гремучая ртуть	$Hg(CNO)_2$	—	−62,8	414

1) Compound; 2) formula; 3) molecular weight; 4) heat of formation; 5) heating value, kcal/kg; 6) acetylene; 7) hydrazoic acid; 8) dicyanogen; 9) prussic acid; 10) nitrous oxide; 11) nitric acid; 12) ozone; 13) calcium azide; 14) copper azide; 15) nitrogen chloride; 16) chlorine dioxide; 17) lead azide; 18) mercury fulminate.

c) Energy of association of atoms into molecules

Many elements normally exist in the form of molecules, for example, H_2, O_2, N_2, F_2, etc. Upon formation of such molecules from free atoms of elements, a large amount of energy is liberated:

$$2H \rightarrow H_2 + 102.7 \text{ kcal/mole}$$

$$2O \rightarrow O_2 + 116.4 \text{ kcal/mole}$$

$$2N \rightarrow N_2 + 169.4 \text{ kcal/mole.}$$
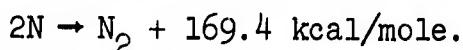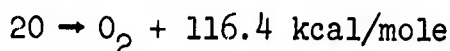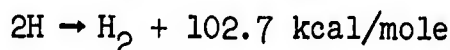
Elements in the atomic state may be obtained in an electric glow discharge, an electric arc, photochemically, and also, evidently, may

be produced by radiation.

Many substances may be obtained in the atomic state in an electric discharge. For example, when a powerful electric discharge is passed through gaseous hydrogen, the molecules dissociate into atoms. Under laboratory conditions, when a stream of molecular hydrogen at a pressure of about 1 mm Hg is passed through an electric glow discharge with a potential difference of 10,000 v, atomic hydrogen is obtained, which may be removed to considerable distances from the discharge zone. At a pressure of 0.5 mm Hg, the concentration of atomic hydrogen drops by a factor of two in comparison with the initial concentration within 1/3 sec [5].

Hydrogen atoms recombine at the surface of several solids. A tungsten wire or thorium oxide located in a stream of cold gas containing atomic hydrogen will become red hot.

This phenomenon is used in engineering for so-called "atomic welding." Atomic hydrogen is obtained in the arc of an electric discharge between tungsten electrodes at atmospheric pressure. To do this, a stream of gaseous hydrogen is forced through the electric arc where 20-25% of the hydrogen molecules dissociate into atoms. The stream obtained is then directed against the surface being welded, which is placed at a distance of 10-15 cm from the arc. The hydrogen atoms recombine at the surface, producing strong local heating. Such high-melting metals as tungsten are processed and fused with the aid of this method. At the same time, the hydrogen prevents oxidation of the metal.

As with hydrogen, atomic oxygen is obtained in an electric discharge. A platinum wire located in a stream of atomic oxygen heats up rapidly and melts owing to the energy released by recombination of oxygen atoms on the surface of the wire.

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Atomic oxygen is extremely active: hydrocarbons instantaneously ignite upon contact with atomic oxygen.

Table 90 gives heats of atomic association for several elements.

TABLE 90

Heats of Association of Atoms into Molecules for Certain Elements [2]

1 Элемент	2 Продукты реакции		3 Теплота реакции	
	4 Состав	5 мол. вес.	6 ккал/моль	7 ккал/кг
8 Водород	H₂	2,02	102,7	51 300
9 Дейтерий	D₂	4,03	104,5	25 930
10 Азот	N₂	28,0	169,4	6 050
11 Углерод	C₂	24,0	127	3 300
12 Кислород	O₂	32,0	116,4	3 630
13 Литий	Li₂	13,9	26,3	1 890
14 Фосфор	P₂	62,0	115,4	1 860
15 Фтор	F₂	38,0	64,6	1 700
16 Сера	S₂	64,1	83	1 300
17 Хлор	Cl₂	70,9	56,9	800

1) Element; 2) reaction product; 3) heat of reaction; 4) composition; 5) molecular weight; 6) kcal/mole; 7) kcal/kg; 8) hydrogen; 9) deuterium; 10) nitrogen; 11) carbon; 12) oxygen; 13) lithium; 14) phosphorus; 15) fluorine; 16) sulfur; 17) chlorine.

The greatest heating value is given by association reactions of atoms of hydrogen, deuterium, oxygen, nitrogen, and carbon. Atoms of the remaining elements yield less heat of reaction upon association.

The application of the energy of atomic association into molecules to reaction engines is hampered by the need for expending a large amount of energy in order to obtain the atoms. At altitudes of 80-90-100 km, however, the atmospheric components such as, for example, oxygen are partially in the atomic state, owing to the effect of the shortwave ultraviolet solar radiation; they do not recombine into molecules since the pressure is so low (at a height of 80 km, atmospheric pressure amounts to 0.01 mm Hg), and no suitable catalyst is present.

In the launching of the "Aerobee" research rocket at the New Mexico proving grounds in 1956, a balloon containing 8.2 kg of nitric oxide was exploded at a height of 96 km [6]. The nitric oxide produced catalytic recombination of the oxygen atoms in the atmosphere, accompanied by a bright flash, and leading to the formation of a cloud of about 5 km in diameter resulting from the liberation of a large amount of energy upon the formation of the oxygen molecules. The glowing cloud remained intact for a 10-min period, and from the earth appeared to be four times the size of the moon.

It has been proposed that the energy of atomic association that may be obtained in the upper atmosphere may be used in special ram-type rocket motors. With the rocket moving at high speed (7-10 times the speed of sound) the rarefied atmosphere will enter at the inlet diffuser of the motor, where it will be compressed to 0.5-1 atm owing to ram action, and then sent on to the combustion chamber, where contact of the oxygen with a catalyst (gaseous NO or heavy metals) should produce energy owing to the association of oxygen atoms into molecules.

At a height of 100 km, the recombination of the oxygen in 1 m^3 of air will liberate 10 kcal; a ramjet engine operating on atomic oxygen will develop very low thrust owing to the low air density.

Many chemical experiments with atomic hydrogen, oxygen, and nitrogen have been carried out under laboratory conditions. Atoms were obtained in discharge tubes at pressures of 0.1-1.0 mm Hg, and under these conditions underwent chemical conversions. The mean lifetimes of the H, O, and N atoms were measured in tenths of a second, and thus the stream containing the atomic hydrogen, oxygen, and nitrogen can be led out to a considerable distance from the discharge point.

Atomic hydrogen possesses exceptional chemical activity. Thus, when atomic hydrogen acts upon certain metals and nonmetals there are

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formed, for example, the hydrides of beryllium, tin, lead, sulfur, phosphorus, and arsenic. Atomic hydrogen with molecular oxygen yields hydrogen peroxide. With ethylene and acetylene, atomic hydrogen causes the formation of high polymers and in this case thus initiates polymerization.

When atomic hydrogen reacts with paraffin hydrocarbons, destructive hydrogenation occurs, resulting in the breaking of the bonds between the hydrogen atoms.

The process of atomic recombination is catalytic. The activity of heterogeneous catalysts for the recombination of hydrogen decreases in the series [5]:

$$Pt > Pb > W > Cr > Cu > Pb > Hg.$$
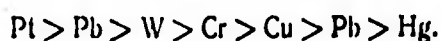
Water is an inhibitor of recombination. The best results are yielded by phosphoric acid in the form of films on surfaces with which atomic hydrogen is in contact.

Interesting reactions may be carried out with atomic nitrogen and oxygen. Thus, the chemical activity of atomic oxygen is considerably greater than even that of ozone.

Nitrogen in the atomic state causes comple.. ...... ns for organic compounds. Thus, when benzene and naphthalene are reacted with atomic nitrogen, the very destructive reactions result in, for example, pyridine, nitryls, quinoline, naphthylamine, and other substances.

Thus, the utilization of hydrogen, oxygen, nitrogen, and other elements in the atomic state presents very considerable scientific interest.

Recently, atomic oxygen and nitrogen have been obtained in the free state in frozen form at $4^{\circ}K$. Upon heating a frozen system to $20\text{-}30^{\circ}K$, the atoms recombine actively, liberating a large amount of heat, accompanied by a flame.

In the United States the Defense Department has devoted a great deal of attention to developing fuels based upon elements in the atomic state and upon radicals. Large groups of scientists have been engaged in such work since 1954.

d) Energy of nuclear reactions

According to the mass-energy equivalence principle

$$E = mc^2,$$

where E is energy, $\underline{m}$ is mass, and $\underline{c}$ is the speed of light.

Upon conversion of the mass of a substance into energy, $2.15 \cdot 10^{13}$ kcal/kg is liberated.

In modern ZhRD, about 2.15-$2.3 \cdot 10^3$ kcal/kg is developed, which is only one ten billionth of the total amount of energy concentrated in the substance.

Thus, it is quite natural to expect an increase in energy output upon transformation of matter.

One of the paths in this direction is the utilization of nuclear energy.

Nuclear transformations are a promising but as yet far from practical energy source for reaction engines [7-9].

Methods of obtaining nuclear energy are discussed in the specialized literature (see, for example, [17]).

We will touch upon this question in connection with an evaluation of the energy available from nuclear reactions as a possible power source for reaction engines.

Three different methods are known for liberating nuclear energy: radioactive decay of unstable nuclei, thermonuclear reactions, and nuclear chain reactions.

The radioactive decay of atomic nuclei of unstable isotopes occurs continuously in all radioactive substances. This process requires no

specific critical mass, and so cannot be regulated. Thus, 1 g of radium develops about 140 cal/hr of heat, and this process can be neither slowed down nor speeded up.

Nuclear reactions accompanied by the liberation of a large amount of energy may occur when the atomic nucleus of an element collides with nuclear components: protons or neutrons.

Table 91 compares nuclear-reaction energies with energies from oxidation reactions.

TABLE 91

Comparison of Various Power Sources for Rocket Motors

1 Процесс	2 Тепловой эффект, ккал/кг	3 Эквивалент сгорающей нефти	4 Удельный импульс, сек	5 Отношение теплового эффекта к $E=mc^2$
6 Энергия окислительных процессов				
$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	3210	0,32 кг	370	$1,5 \cdot 10^{-10}$
$C_nH_{2n} + O_2 \rightarrow CO_2 + H_2O$	2270	0,22 »	290	$1,1 \cdot 10^{-10}$
$C_xH_yO_2N \rightarrow CO + CO_2 + H_2O + N_2$ 7 (порох)	1200	0,12 »	210	$6 \cdot 10^{-11}$
8 Энергия ассоциации атомов				
$H + H \rightarrow H_2$	51 000	5,1 кг	1600	$2,4 \cdot 10^{-8}$
$N + N \rightarrow N_2$	6050	0,6 »	530	—
9 Энергия ядерных реакций				
$H + Li^7 \rightarrow 2He$	$5,1 \cdot 10^{10}$	5100 m	$1 \cdot 10^6$	—
$4H \rightarrow He$	$1,62 \cdot 10^{11}$	1620 »	$2,5 \cdot 10^6$	$7,5 \cdot 10^{-3}$
$D \rightarrow He$	$3,9 \cdot 10^{10}$	3900 »	—	—
10 $U^{235} \rightarrow$ продукты деления	$1,57 \cdot 10^{10}$	1570 »	$1,2 \cdot 10^6$	$4,31 \cdot 10^{-7}$
11 1 кг воды → образование гелия из дейтерия воды	$4 \cdot 10^6$	0,4 »	$1,25 \cdot 10^4$	—
12 Превращение массы в энергию				
$E = mc^2$	$2,15 \cdot 10^{13}$	$2,15 \cdot 10^6$	$3 \cdot 10^7$	1,0

1) Process; 2) thermal efficiency, kcal/kg; 3) petroleum-combustion equivalent; 4) specific impulse, sec; 5) ratio of thermal efficiency to $E = mc^2$; 6) energy of oxidizing processes; 7) (powder); 8) energy of atomic association; 9) energy of nuclear reactions; 10) $U^{235} \rightarrow$ fission products; 11) 1 kg water → formation of helium from the deuterium of the water; 12) conversion of mass into energy.

Specific impulse is computed in kilograms per kg of fuel converted in 1 sec, and is found from the formula

$$P = 9.33 \sqrt{0.4\,H},$$

where H is the thermal efficiency of the reaction in kcal per kg of fuel. For nuclear reactions, it is necessary to utilize an intermediate working fluid, which is heated by the nuclear reaction. In this case, in practice, the specific impulse from a nuclear reaction with uranium will amount to not 1,000,000 sec, but some 1000-3000 sec per kg of working fluid.

In nuclear chain reactions in which neutrons participate, a neutron colliding with a nucleus is absorbed by the nucleus, which then ejects one or several new neutrons. At the same time, new nuclei are formed. All known nuclear chain (i.e., selfpropagating), reactions that liberate energy and increase the number of neutrons take place with heavy nuclei.

For a nuclear reaction to take place, a certain critical mass must be present. It is only under these conditions that the nuclei are able to capture neutrons with sufficient effectiveness.

For the chemically pure uranium isotopes U^{233} and U^{235}, as well as for plutonium Pu^{239}, the critical mass takes the form of a sphere having a radius of several centimeters. The action of atomic explosives is based upon the formation of a critical mass at the required instant by bringing together two component parts of the critical mass. Following this, an explosion occurs within about 10^{-6} sec.

The nuclear reaction in uranium, which under appropriate conditions will occur extremely rapidly (10^{-6} sec), may be slowed down by means of a special "moderator." Such moderators are chemically pure graphite, heavy water, and certain other substances.

When a moderator is used, the atomic energy is liberated at a con-

siderably lower rate. This is the only way in which it may be used in reaction engines. Even here, however, there are extremely great difficulties. The particles formed in a nuclear reaction travel at high speeds. Their direction of motion is irregular, however, and the speed of the particles is extremely high (of the order of 10,000 km/sec, while in reaction engines, the exhaust velocity ranges from 2-3 km/sec), and thus their ejected mass cannot be used directly to create thrust.

The first experimental atomic rocket engine in the USA used liquid helium as the working fluid during the 1959 experiments. Liquid hydrogen will be used in the future for the motor. In operation, this motor reached a working-fluid exhaust velocity of the order of 10 km/sec, corresponding to a specific thrust of about 1000 sec. In a conventional rocket motor using liquid oxygen and kerosene, the exhaust velocity of the gases amounts to about 3 km/sec, and the specific impulse to about 300 sec.

In a nuclear rocket motor, it is necessary to control the process of atomic fission, and this is normally done with the aid of graphite rods introduced into the U^{235} mass to regulate the intensity of the nuclear reaction by capturing neutrons capable of causing further fission of the uranium nuclei. In addition to helium and hydrogen, recommended working fluids are water, ammonia, liquefied hydrocarbon gases, and, finally, air.

In the final analysis, the effectiveness of the rocket propellant employed is characterized by the velocity with which the reaction products leave the motor nozzle. The speed developed by the rocket at the final instant of propellant combustion is proportional to the velocity with which the combustion products flow out of the motor nozzle [9].

In order to apply nuclear fuels to reaction engines, it is necessary to overcome several substantial technical difficulties. These dif-

ficulties are primarily associated with cooling the nuclear reactor under reaction-engine operating conditions, as well as with the protection of personnel against harmful radiation.

Atomic engines will be utilized in the final stages of cosmic multistage rocket powerplants in order to avoid setting up hazards in the launch area.*

The utilization of atomic rocket motors requires very heavy structures as biological shielding against harmful reactor radiation.

For spacecraft rockets designed for flights within the solar system and beyond, weighing more than modern ocean liners, the creation of such shielding is quite practical. Such protection has been realized on submarines and surface vessels using atomic engines.

e) Energy from ion and photon motors

In the literature, there are discussions of new types of motors in which the thrust is created by ejecting ions from the motor in an ion engine, or by converting matter into electromagnetic waves (light quanta) radiated from the engine in a single direction.

The ion motor employs a charged-particle generator which uses, for example, a powerful electric arc to form ions, creating a so-called plasma. The most suitable substance for ion formation is cesium, which has a very low ionization energy.

The ionized particles obtained are delivered to an accelerator where they are speeded up in an electromagnetic field which accelerates and focuses the ion beam. The change in momentum of the accelerated particles leads to the appearance of thrust.

The impulse of such a motor is of the order of 1000 kg per sec per kg of working fluid; the total thrust, however, is low and is measured in the kilograms and tens of kilograms.

An ion motor cannot overcome the force of gravity, and will be em-

ployed for guided space flights.

Electric power may be furnished to an ion motor by an atomic electric power plant or, possibly, solar batteries.

The photon rocket motor is based upon the conversion of matter into light energy, i.e., there is a conversion of mass into the energy of electromagnetic radiation.

As is known, light radiation has a definite pressure, depending upon temperature. The radiation pressure of a perfect black body is found from the equation

$$P = 1.927 \cdot 10^{-21} \ T^4 \ kgf/cm^2.$$

At a temperature of $100,000^{\circ}$, the light pressure will be of the order of $0.2 \ kgf/cm^2$, while at $1,000,000^{\circ}$, it will be about 2000 kgf/cm^2. This makes it possible to obtain a thrust of about 20,000 tons from an area of $1 \ m^2$.

A photon motor should consist of a chamber that is transparent to radiation from one direction. A thermonuclear process should be going on in the motor chamber, causing the matter to be heated to a temperature of several tens of millions of degrees, accompanied by powerful radiation.

Many major obstacles lie in the way of a solution to this problem.

2. General Characteristics of Fuels for Liquid Reaction Engines

In engineering, fuels are defined as substances or mixtures of substances capable of releasing a considerable amount of energy during chemical-reaction processes, which are normally described by the general term "combustion."

Fuels for liquid reaction engines represent systems that under specific conditions are able to convert at considerable speed to other, less active systems, with the liberation of a large amount of heat and the formation of a considerable number of gaseous products, owing to

which it is possible to convert the potential energy concentrated in the initial substance or substances into heat energy, and then into the kinetic energy of motion of the gases creating the thrust.

Fuels may be classified into the following three types according to the method of application:

a) bipropellants, for which the oxidizer and combustible are supplied separately;

b) monopropellants, containing within themselves all elements required for combustion.

The classification of reaction-engine fuels by composition is based upon the properties of the components, which determine the characteristics of the fuel as a whole. There is still no firmly established classification of fuels, and the details of this classification are arranged rather arbitrarily by various authors.

It seems to us desirable at the present time to make the following classification of bipropellants (supplied separately) for liquid reaction engines, depending upon the oxidizers used.

1. Fuel base: liquid oxygen.

2. Fuel base: nitric acid and oxides of nitrogen.

3. Fuel base: liquid fluorine and other oxyfluorides.

4. Fuel base: concentrated hydrogen peroxide.

5. Fuel base: tetranitromethane and other nitro derivatives.

At present, the oxidizers most frequently employed in practice are: nitric acid, oxides of nitrogen, liquid oxygen and, less frequently, concentrated hydrogen peroxide; the most common combustibles are kerosene and other petroleum products, as well as alcohols, amines, hydrazine and its derivatives. The combination of oxidizer and combustible is called a "propellant mixture" or simply a "propellant." In the majority of cases, the propellant mixture contains 75-85% oxidizer

and 15-25% combustible. Fuel based upon liquid oxygen and 75% ethyl alcohol represents an exception. Such a propellant contains 40-45% dilute alcohol and 55-60% oxygen [8,9].

Propellant properties and the possibility of using a propellant in a given engine system are to a large degree determined by the nature of the oxidizer with respect to its specific properties.

In oxygen-base propellants, alcohols are used as the combustible, although it is also possible to use petroleum products for this purpose. In order to start engines using these propellants, the propellant is forcibly ignited by means of a pyrotechnical charge or a starting nozzle.

In fuels based upon nitric acid and hydrogen peroxide, the combustibles employed are amines, aromatic and unsaturated oxy compounds that form hypergolic combinations with these reagents.

Liquid monopropellants differ from separately supplied fuels in that the oxidizer and combustible are stored in a single tank, and supplied together to the combustion chamber. These propellants have an advantage in that there is no need to use two tanks, which results in an engine structural simplification. In addition, the propellant is supplied to the combustion chamber in ready-mixed form which improves combustion conditions.

Monopropellants mainly consist of liquid mixtures of oxidizers and combustibles or individual liquid explosives. This form of propellant, however, is far from having a secure position in rocket technology owing to the fact that such propellants are very explosive systems. In this connection, combustion or explosive decomposition in the combustion chamber of a reaction motor may penetrate to the propellant tank through piping (or the air) and end in an explosion. At the present time, only low-efficiency monopropellants having a low heat of com-

bustion are used, since these systems are not very liable to explosion [9].

Monopropellants are systems potentially able to decompose explosively and thus they differ chemically from separately supplied fuels.

Fuels for liquid reaction engines are chosen with an eye to certain energy, physicochemical, and operational properties.

Let us consider the basic specifications applicable to fuels.

1. Fuels should have high heating yields, evolve large quantities of gases with optimum physical properties of the combustion products so that the combination of these quantities will produce the maximum combustion-product exhaust velocity. Each of these characteristics taken separately in isolation from the remaining characteristics cannot characterize fuel quality with sufficient accuracy or completeness.

2. A fuel should also possess the greatest possible specific gravity; in combination with other properties, this should provide maximum speed and range for the rocket.

3. The propellant components should be good coolants, since in the majority of cases they will be used at the same time to cool the motor walls. In this case, the propellant should have sufficiently high heat capacity, thermal conductivity, and in many cases, a high latent heat of vaporization if the propellant components are to be utilized to cool the inside walls of the motor.

4. The propellant should ignite easily and surely in the combustion chamber from a special primer or upon contact of the oxidizer with the combustible.

5. Hypergolic fuels are subject to the requirement that the ignition lag should if at all possible not exceed 0.02-0.03 sec. Here it is desirable that ignition should not be of explosive nature, and that the pressure developing upon ignition of the propellant does not con-

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siderably exceed that at which the basic combustion process occurs.

6. Mixed propellants should as far as possible possess high burning rates, since the propellant does not stay in the engine very long, and thus combustion should be stable.

7. The propellants should possess adequate chemical and physical stability, so as to permit extended storage. This requirement, however, does not exclude the use of chemically unstable substances, if methods are found to stabilize them, or of physically unstable oxidizers such as liquid oxygen.

8. As far as possible, a propellant should not corrode standard structural materials (steel, etc.). Where this is not the case, special structural materials must be used for the rocket motors: aluminum or stainless steel. This requirement, however, does not exclude the present-day use of such oxidizers as concentrated nitric acid and hydrogen peroxide, which require special materials for storage.

9. A propellant and propellant components for rocket motors should have low pour points (-40°, and in some cases -60°), to prevent their solidification when the motor operates in the upper atmosphere (jet aviation with ZhRD) or upon storage during the winter. At the same time it is desirable that propellant components not boil at temperatures below $80\text{-}100^{\circ}$, so as to eliminate the need for special measures to prevent evaporation of these materials during storage. All of this, however, does not prevent the utilization in special cases of materials freezing at higher temperatures or boiling at lower temperatures.

10. Propellants and propellant components for rocket motors should as far as possible not be highly toxic, a condition which complicates handling of the propellants.

11. Mixed-propellant components and propellants should as far as possible have low surface tension and low true viscosity, guaranteeing

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their pumpability and good dispersion in the motor combustion chamber.

12. Propellants should not present danger of explosion during storage, and should not explode in the rocket motor under normal operation.

13. The raw-material and industrial base should provide for the manufacture of propellants for rocket motors. Speaking plainly, rocket propellants should be plentiful and cheap.

This entire set of specifications given above should not be considered as a law from which no deviations should be made. In individual cases, good propellant qualities, availability, or other special characteristics may make it desirable to use a given propellant although it may possess several undesirable properties. In other cases, although a propellant may have excellent energy characteristics, it may prove to be unfeasible owing to unfavorable operating qualities.

3. The Concept of Determining the Stoichiometric Composition, Density, Specific Volume of Combustion Products, and Heating Value of a Propellant

For a preliminary characterization of a propellant, it is necessary to determine the stoichiometric composition of the propellant mixture and the composition of the combustion products, the propellant density, the specific volume of the combustion products, the propellant heating value, and to estimate the combustion-product exhaust velocity. The full calculation for ZhRD propellants is given in the book of M. I. Shevelyuk [10].

a) Determining the stoichiometric composition of a propellant

As an example, let us examine propellant mixtures consisting of cyclohexane, alcohol, and oxygen.

Complete combustion of these propellants takes place according to the equations:

$$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O;$$

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$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O.$$
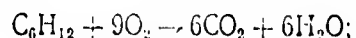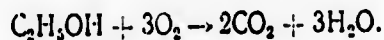
The stoichiometric composition of a propellant mixture is found as the quotient resulting from division of the molecular weight of each component multiplied by the number of moles, by the total molecular weight of the propellant mixture:

$$C_6H_{12} = \frac{M_{C_6H_{12}}}{M_{C_6H_{12}} + 9M_{O_2}} \cdot 100 = \frac{84}{84 + 9 \times 32} \cdot 100 = 22,0\%;$$
$$O_2 = \frac{9 \times 32}{84 + 9 \times 32} \cdot 100 = 78\%.$$

For an alcohol-oxygen propellant, the calculation yields the following composition: O_2 — 67.6% and C_2H_5OH — 32.4%.

Less oxygen is required to burn alcohol, since the molecule is already partially oxidized.

In general form, the combustion reaction may be written as follows*:

$$C_aH_bN_cO_e + \left(2a + \frac{b}{2} - e\right) \times O \rightarrow a\,CO_2 + \frac{b}{2}H_2O + \frac{c}{2}N_2,$$
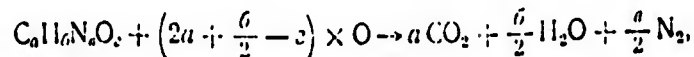
where a, b, c, and d are the number of corresponding atoms in the molecule.

The complete combustion reaction equation for cyclohexane and nitric acid is found from the stoichiometric equation:

$$C_6H_{12} + 7,2\,HNO_3 \rightarrow 6CO_2 + 9,6H_2O + 3,6\,N_2.$$

The propellant composition is:

$$C_6H_{12} = \frac{84}{84 + 7,2 \times 63} \cdot 100 = 15,7\%;$$
$$HNO_3 = \frac{7,2 \times 7,2 \times 63}{84 + 7,2 \times 63} \cdot 100 = 84,3\%.$$

The stoichiometric composition is not optimal since a combustion process in liquid reaction engines normally takes place with a negative oxygen balance, i.e., with an excess of combustible ($\alpha = 0.80$-0.90), which results in maximum exhaust velocity and specific thrust.

_____

*b = b, c = c, d = d.

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b) Density of propellant mixture

The density of a propellant mixture is an important characteristic, since it is this factor that determines the supply of propellant in the tanks. It must be kept in mind, however, that in rocket motors the propellant components — oxidizer and combustible — are located in separate tanks, and thus in this case, we arbitrarily define the propellant-mixture density as the value that would be obtained if the oxidizer and combustible were mixed in one tank.

The density of a multicomponent propellant is found by dividing the total molecular weight of the propellant-mixture components by their total specific volume:

$$\rho = \frac{n_1 M_1 + n_2 M_2 + \ldots n_m M_m}{\frac{n_1 M_1}{\rho_1} + \frac{n_2 M_2}{\rho_2} + \ldots + \frac{n_m M_m}{\rho_m}},$$

where $\underline{n}$ is the number of moles of the substances making up the propellant mixture; M is the molecular weight of the propellant components; ρ is the density of the propellant components.

Let us find the density of the two propellants given above: cyclohexane-oxygen and cyclohexane-nitric acid:

For the cyclohexane-oxygen mixture, $\rho = \dfrac{1 \times 84 + 9 \times 32}{\frac{1 \times 84}{0,7934} + \frac{9 \times 32}{1,14}} = 1,05.$

For the cyclohexane-nitric acid mixture, $\rho = \dfrac{1 \times 84 + 7,2 \times 63}{\frac{1 \times 84}{0,7934} + \frac{7,2 \times 63}{1,5129}} = 1.32.$

High density is a factor that is favorable in propellant mixtures, since more heavy fuel than light fuel can be stored in the tanks of a rocket motor, all other properties remaining the same.

c) Specific volume of gaseous combustion products

The gaseous products which form upon combustion of a propellant mixture in the combustion chamber form the working fluid which used to convert the thermal energy of the propellant into the kinetic energy of the gases exiting at high velocity from the motor nozzle, and creat-

ing the thrust.

The most efficient fuel, if it does not form gases, will create no thrust whatsoever upon combustion in the motor.

The "specific gas evolution" is used to characterize the gas-forming ability; this term is defined as the amount of gaseous products forming upon combustion of 1 kg of propellant, adjusted for normal conditions, i.e., 0° and a pressure of 760 mm Hg. The specific volume is computed by multiplying the volume occupied by a gram-molecule (under normal conditions, 22.41 liters) by the number of moles forming, and dividing by the total molecular weight of the propellant mixture:

$$v_0 = \frac{22.4\,(n_1 + n_2 + \ldots n_m)}{m_1 M_1 + m_2 M_2 + \ldots m_m M_m} \cdot 1000,$$

where v_0 is the specific volume of gaseous combustion products; n is the number of gram-molecules forming upon combustion of the propellant; m is the number of moles in the propellant-mixture components; the M are the molecular weights of the components.

Let us examine the specific volume of the combustion products formed from the propellants considered above.

For a mixture of cyclohexane and oxygen

$$v_0 = \frac{22.4\,(6 + 6)}{84 + 9 \times 32} \cdot 1000 = 722 \text{ liters/kg.}$$

For a mixture of cyclohexane and nitric acid

$$v_0 = \frac{22.4\,(6 + 9.6 + 3.6)}{84 + 7.3 \times 63} \cdot 1000 = 794 \text{ liters/kg.}$$

d) Heating yield of propellant

The heating yield of a propellant (H) is one of the most important characteristics of a propellant; upon it depends the thrust developed by the motor, since reaction motors operate on the principle of converting the thermal energy of the propellant into the kinetic energy of the combustion products formed upon combustion, which are in the

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gaseous state. The heating yield is associated with the chemical composition of the propellant. The heating yield is the name given to the amount of heat liberated by a rocket propellant upon combustion of 1 kg of propellant mixture, i.e., mixture of oxidizer and combustible.

The heating yield is a true physical characteristic of a propellant where its absolute value depends solely upon propellant composition, and not upon the combustion conditions.

A propellant's upper-limit heat yield is a scientific and engineering standard quantity; it corresponds to the condition in which all of the water vapor in the combustion products and residual products are cooled to 18°. Under actual combustion conditions in a motor, the water formed escapes in the form of vapors.

In order to approximate to practical conditions, the heating yield is found under conditions in which the water vapor remains in the gaseous state, and it is assumed that the reaction products are cooled to the standard temperature of $+18^\circ$. When certain types of rocket propellants are burned, oxides and fluorides of metals and non-metals may form (for example, B_2O_3, Al_2O_3, AlF_3) requiring large expenditures of heat for vaporization, and thus in talking of the lower heating yield of jet fuels, whose combustion products contain high-boiling substances, we have in mind conditions under which the high-boiling reaction products are in the vapor state.

A calculation of the heating yield of a rocket propellant is carried out on the basis of the well-known Hess thermodynamic law according to which the amount of heat evolved or absorbed during chemical processes depends solely upon the initial and final states of the system of bodies participating in these processes.

In thermochemistry, we mean by the initial and final states of the system of bodies participating in a reaction, the sum of the heats

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of formation of the substances taken for the reaction and obtained after the combustion reaction.

Consequently, in order to carry out thermal calculations, it is necessary to know the heats of formation of the substances taken for the reaction and forming after the reaction, as well as the total molecular weight of the propellant mixture.

The calculation is carried out in accordance with the formula

$$H = \frac{(n_1 q_1 + n_2 q_2 + \ldots n_n q_n) - (m_1 q_1' + m_2 q_2' + \ldots m_m' q_m')}{m_1 M_1 + m_2 M_2 + \ldots m_m M_m} \cdot 1000,$$

where H is the heating yield (kcal/kg); $\underline{m}$ is the number of molecules of substances entering into the mixture; the M are the molecular weights of the substances taken up; $\underline{n}$ is the number of molecules of the substances forming; the $\underline{q}$ are the heats of formation of the substances forming; the q' are the heats of formation of the substances taken up.

Let us examine the heating yield of a propellant consisting of a stoichiometric amount of cyclohexane and liquid oxygen, and burning in accordance with the reaction

$$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O.$$

The heat of formation of C_6H_{12} is 40.26 kcal/mole. The latent heat of vaporization for liquid oxygen is 1.632 kcal/mole, the heat capacity is 6.9 cal/mole·degree. Hence the heat of vaporization for liquid oxygen, allowing for heating from the boiling point of −182 to +18° is:

$$i = 1,632 + 0,0069 \cdot 200 = 3,01 \text{ kcal/mole}.$$

The heat of formation of CO_2 is 94.05 kcal/mole and for H_2O (in the vapor state) 57.8 kcal/mole.

$$H = \frac{(6 \times 94,05 + 6 \times 57,8) - (40,26 \times 1 + 3,01 \times 9)}{84 + 9 \times 32} \times 1000 = 2270 \text{ kcal/kg}.$$

Aluminum burns in oxygen according to the reaction:

of formation of the substances taken for the reaction and obtained after the combustion reaction.

Consequently, in order to carry out thermal calculations, it is necessary to know the heats of formation of the substances taken for the reaction and forming after the reaction, as well as the total molecular weight of the propellant mixture.

The calculation is carried out in accordance with the formula

$$H = \frac{(n_1q_1 + n_2q_2 + \dots n_nq_n) - (m_1q_1' + m_2q_2' + \dots m_m'q_m')}{m_1M_1 + m_3M_3 + \dots m_mM_m} \cdot 1000,$$

where H is the heating yield (kcal/kg); $\underline{m}$ is the number of molecules of substances entering into the mixture; the M are the molecular weights of the substances taken up; $\underline{n}$ is the number of molecules of the substances forming; the $\underline{q}$ are the heats of formation of the substances forming; the q' are the heats of formation of the substances taken up.

Let us examine the heating yield of a propellant consisting of a stoichiometric amount of cyclohexane and liquid oxygen, and burning in accordance with the reaction

$$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O.$$

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$$i = 1,632 + 0,0069 \cdot 200 = 3,01 \text{ kcal/mole}.$$

The heat of formation of CO_2 is 94.05 kcal/mole and for H_2O (in the vapor state) 57.8 kcal/mole.

$$H = \frac{(6 \times 94,05 + 6 \times 57,8) - (40,26 \times 1 + 3,01 \times 9)}{84 + 9 \times 32} \times 1000 = 2270 \text{ kcal/kg}.$$

Aluminum burns in oxygen according to the reaction:

$$2Al + 1\frac{1}{2}O_2 \rightarrow Al_2O_3 + 402 \text{ kcal.}$$

The upper-limit heat yield of this propellant is

$$H = \frac{402}{101.4} \cdot 1000 = 3940 \text{ kcal/kg.}$$

The lower-limit yield will be obtained if we make a correction for the latent heat of fusion and vaporization of aluminum oxide. Aluminum oxide melts at a temperature of 2050° and boils at 2980°; the latent heat of fusion is 8.2 kcal/mole and the latent heat of vaporization is 171.1 kcal/mole, so that the lower-limit heat yield, i.e., the heating yield where the Al_2O_3 is in the vapor state, will equal:

$$H_{\text{H}} = \frac{402 - 8.2 - 171.1}{101.4} \cdot 1000 = 2220 \text{ kcal/kg.}$$

Knowing the heating yield of the propellant and the composition of the combustion products, it is possible to make an approximate determination of the combustion-product exhaust velocity and the specific thrust. To do this, we find the thermal efficiency according to the combustion-product composition.

Thus, the heating yield of a kerosene-nitric acid (98%) propellant is 1425 kcal/kg; the thermal efficiency is 0.360 for a combustion-chamber pressure of 20 atm. Hence the exhaust velocity and specific impulse will equal:

$$u = 91.53 \cdot \sqrt{0.360 \cdot 1425} = 2060 \text{ m/sec};$$
$$p = 9.33 \cdot \sqrt{0.360 \cdot 1425} = 210 \text{ sec.}$$

This method for obtaining an estimate of specific thrust produces errors in comparison with experimental values of about 2.5%, and may be employed for first rough estimates of propellant quality.

A calculation of propellant combustion temperature is of greater complexity than a calculation of propellant heating yield, since it is necessary to allow for the dissociation of the combustion products and the corresponding changes in composition and heats of formation of the

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combustion products. The combustion temperature found with no allowance for dissociation does not reflect the physical pattern of the process.

Detailed calculations for rocket-propellant combustion processes are given in the books of V.I. Fedos'yev and G.B. Sinyarev [9] and M.I. Shevelyuk [10].

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Manu- script Page No.	[Footnote]
341	The United States expects to make an atomic rocket motor by 1970.

Manu- script Page No.	[List of Transliterated Symbols]
329	ЖРД = ZhRD = zhidkostnyy reaktivnyy dvigatel' = liquid reaction-thrust engine
353	н = n = nizshaya = lower-limit

Chapter 2
CHARACTERISTICS OF LIQUID-REACTION ENGINE FUEL PROPERTIES

The properties that rocket propellants should have are determined by the requirements imposed during development and construction of the rockets. The specifications reduce to two main requirements: for minimum initial weight, the rocket should attain maximum horizontal range or, with vertical launching, maximum ascent altitude, as well as maximum velocity at the end of the powered segment, i.e., when all of the propellant is burnt up.

Methods for evaluating rocket propellants follow from these requirements. Propellant quality may be characterized in terms of speed, range, or height of ascent of the rocket.

The maximum speed of a single-stage rocket at the end of the powered segment is determined from the equation [1]

$$v = u \cdot \ln (1 + \rho \cdot \gamma) - \bar{g} \cdot \tau, \qquad (1)$$

where v is the maximum rocket speed; u is the combustion-product exhaust velocity; γ is a structural factor for the rocket — the ratio of the tank volume to the weight of the rocket without propellant; $\bar{g}$ is the mean gravitational acceleration; τ is the flight time for the powered segment; ρ is the propellant density.

The combustion-product exhaust velocity is found from the formula

$$u = 91{,}53 \sqrt{\eta_t \cdot H}, \qquad (2)$$

where H is the propellant heating value; η_t is the thermal efficiency, which depends upon the combustion-product composition and the pres-

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sure in the chamber (more accurately, the degree of expansion), as follows from the data given below:

Number of atoms in a molecule of combustion products	$p/p_0 = 25$	$p/p_0 = 100$
2	0.512	0.641
3	0.369	0.482
4	0.275	0.369
5	0.218	0.298

The combustion-product exhaust velocity, calculated from Eq. (2), may differ from the value obtained in practice, on the average, by ± 2%. Thus, the theoretical velocity may be used as a preliminary propellant characteristic [1].

In order to simplify the calculations involved in a comparison of propellant quality, the earth's gravitational force may be neglected. In this case, we obtain the so-called "ideal" maximum rocket speed:

$$v = u \ln (1 + d_m \gamma);$$
$$v = g R_{y\lambda} \ln (1 + d_m \gamma).$$

The maximum speed of a multistage rocket having completely identical stages will take the form:

$$v = n \cdot u \ln (1 + d_m \gamma),$$

where n is the number of stages (2, 3, etc.).

Maximum rocket range is proportional to the square of the speed.

According to Zenger's formula [2] it is proportional to the third power of the combustion-product exhaust velocity:

$$S \sim \frac{0.17}{10^6} \cdot u^3 \left[\ln (1 + d_m \gamma) \right]^3.$$

This relationship cannot be considered accurate, however.

The heating value, combustion-product exhaust velocity, and specific thrust are primary propellant characteristics. Taken in a specific mathematical relationship with an allowance for the specific

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gravity, they may characterize propellant efficiency.

As possible rocket-propellant combustibles, we may consider those elements and their compounds that in combination with oxidizers (oxygen, fluorine, etc.) give relatively high low-limit heat yields for the propellant mixture (no less than 1500-2000 kcal/kg) [2-5].

The initial evaluation of the energy properties of proposed propellants is carried out with no consideration of their operational qualities.

Table 92 gives data on the heating yields for several propellant

TABLE 92

Heating Yield and Calculated Specific Impulse for Propellants Based upon Oxygen and Several Simple Combustibles.* [1, 3-5]

1) Элемент	2) Окисел	3) Теплопроизводительность, ккал/кг		6) Удельный импульс, сек	
		4) высшая	5) низшая	$p/p_0 = 25$	$p/p_0 = 100$
7) Водород	H_2O	—	3215	322	370
8) Углерод	CO_2	2140	2140	263	300
9) Литий	Li_2O	4760	1460	216**	247
10) Бериллий	BeO	5400	210 Отрицательная	—	—
11) Бор	B_2O_3	4340	3060	240	282
12) Алюминий	Al_2O_3	3840	2220	201	240
13) Магний	MgO	3630	Отрицательная	—	—
14) Кремний	SiO_2	3420	2060	253	—
15) Фосфор	P_2O_5	2540	—	—	—
16) Кальций	CaO	2710	420	—	—
17) Скандий	Sc_2O_3	2970	—	—	—
18) Титан	TiO_2	2730	—	—	—
19) Ванадий	V_2O_5	2050	—	—	—
20) Цирконий	Zr_2O_3	2100	—	—	—

*Hydrocarbon propellants using oxygen give a heat value of 2270 kcal/kg, and a calculated specific impulses of 270 and 310 sec.

**According to recent data from the foreign literature [5a], the specific impulse for the Li + O_2 system comes to 318 sec, with p/p_0 = 30. This question should be checked in connection with the contradictory data on the heats of formation of gaseous Li_2O.

1) Element; 2) oxide; 2) oxide; 3) heating yield, kcal/kg; 4) high; 5) low; 6) specific impulse, sec; 7) hydrogen; 8) carbon; 9) lithium; 10) beryllium; 11) boron; 12) aluminum; 13) magnesium; 14) silicon; 15) phosphorous; 16) calcium; 17) scandium; 18) titanium; 19) vanadium; 20) zirconium.

mixtures made up of certain elements and oxygen, and the specific impulses that would be obtained upon combustion of such a propellant in a rocket motor at 25 and 100 atm and combustion-product expansion to a pressure of 1 atm.

The heating yield of propellant mixtures based upon elements and oxygen is found from the heats of formation of the corresponding oxides, and the lower-limit heat yield by deducting the heat expended upon vaporization of the oxides.

Such elements as beryllium and magnesium develop large quantities of heat upon combustion. This amount of heat, however, is insufficient for total vaporization of the combustion products, which should form the working fluid in the exhaust process. Boron and aluminum provide high heating values when used in propellant mixtures. In this case, however, pentatomic combustion products are formed; their thermal efficiency upon expulsion is low: $\eta_t = 0.22$-0.37. Thus the specific impulse does not exceed that available from propellants based upon hydrocarbons and oxygen.

The remaining elements, not shown in Table 92, have poorer energy indices.

In addition to oxygen, it is theoretically possible to employ fluorine as an oxidizer, since of all the known elements capable of functioning as oxidizer, oxygen and fluorine alone yield propellant mixtures with high heat yields.

The energy properties of propellant mixtures based upon several elements and fluorine are shown in Table 93.

Fluorine, used as an oxidizer in conjunction with the majority of elements (excluding carbon) is able to provide a propellant having better indices than propellants using an oxygen oxidizer. Fluorides have lower boiling points than oxides, and several of the fluorides

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TABLE 93

Energy Indices for Propellants Based upon Fluorine in Combination with Several Simple Combustibles* [3, 5, 6].

1) Элемент	2) Формула фторида	3) Теплопроизводительность, ккал/кг		6) Удельный импульс, сек	
		4) высшая	5) низшая	$p/p_s = 25$	$p/p_s = 100$
7) Водород	HF	3190	3190	374	420
8) Углерод	CF₄	1830	2100	218	255
9) Литий	LiF	5650	3200	379	424
10) Бериллий	BeF₂	4830	4000	358	—
11) Бор	BF₃	3790	3790	305	348
12) Алюминий	AlF₃	3700	3350	284	—
13) Магний	MgF₂	4230	2700	204	335
14) Кремний	SiF₄	3550	3550	260	302
15) Фосфор	PF₅	2500	—	—	—
16) Кальций	CaF₂	3720	—	—	—
17) Титан	TiF₄	2990	2000	236	—
18) Цирконий	ZrF₄	—	2600	222	—

*Hydrocarbon fuels with fluorine give heat yields of 2440 kcal/kg and calculated impulses of 290 and 330 sec.

1) Element; 2) fluoride formulas; 3) heating yield, kcal/kg; 4) high; 5) low; 6) specific impulse, sec; 7) hydrogen; 8) carbon; 9) lithium; 10) beryllium; 11) boron; 12) aluminum; 13) magnesium; 14) silicon; 15) phosphorous; 16) calcium; 17) titanium; 18) zirconium.

are gases under normal conditions. Thus, there is a decrease in the inefficient expenditure of heat on vaporization of combustion products, and the major portion of the energy freed is converted into mechanical work. At the same time, we should note that despite its excellent energy indices fluorine has drawbacks as an oxidizer that complicate its application. The gravest of these are high toxicity and low boiling point.

Table 94 gives data for the heat of formation of oxides and fluorides in the solid and gaseous states. Figure 125 illustrates the heating yield and specific thrust (specific impulse) of propellants based upon several elements with oxygen and fluorine, and the heat capacity of the combustion products for a combustion-chamber pressure of 22 atm, and expansion of the combustion products to

TABLE 94

Heats of Formation of Oxides and Fluorides in Solid and Gaseous State [4].

1) Элемент	2) Формула окисла или фторида	3) Мол. вес.	4) Теплота образования, ккал/г-моль	
			5) в твердом состоянии	6) парообразном состоянии
7) Водород	H_2O	18,02	—	57,78
8) Литий	Li_2O	29,88	142,6	43,68
9) Бериллий	BeO	25,02	143	—
10) Бор	B_2O_3	60,64	305,4	214,8
11) Алюминий	Al_2O_3	101,94	402	222,7
12) Магний	MgO	40,32	143,8	—
13) Кремний	SiO_2	60,06	210	79,1
14) Фосфор	P_2O_5	141,96	360,0—367,0	350
15) Кальций	CaO	56,08	151,7	29
16) Углерод	CO_2	44,01	—	94,052
17) Водород	HF	20,01	—	64,2
18) Литий	LiF	25,94	146,3	82,7
19) Бериллий	BeF_2	47,02	241,8	186,8
20) Магний	MgF_2	63,32	263,8	176,1
21) Алюминий	AlF_3	83,47	355,7	281,3
22) Бор	BF_3	67,82	—	267,0
23) Кремний	SiF_4	104,06	—	373,0
24) Кальций	CaF_2	78,08	290	—
25) Углерод	CF_4	88,01	—	218 (187)

1) Element; 2) formula of oxide or fluoride; 3) molecular weight; 4) heat of formation, kcal/g-mol; 5) in solid state; 6) in gaseous state; 7) hydrogen; 8) lithium; 9) beryllium; 10) boron; 11) aluminum; 12) magnesium; 13) silicon; 14) phosphorous; 15) calcium; 16) carbon; 17) hydrogen; 18) lithium; 19) beryllium; 20) magnesium; 21) aluminum; 22) boron; 23) silicon; 24) calcium; 25) carbon.
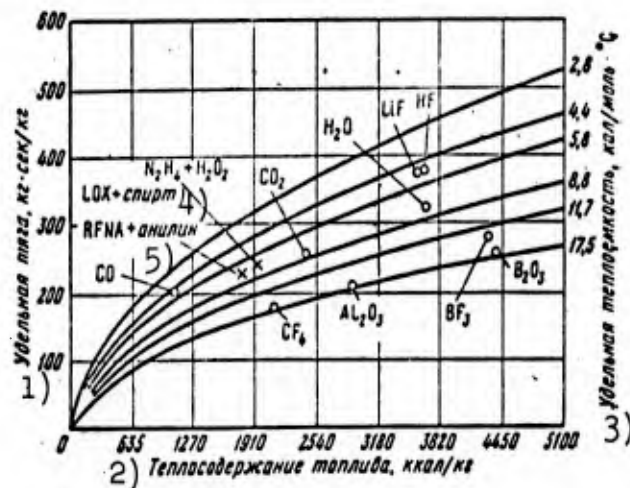
Fig. 125. Specific thrust for several propellants as a function of heat content and heat capacity of combustion products. 1) Specific thrust, kg·sec/kg; 2) heat content of propellant, kcal/kg; 3) specific heat capacity, cal/mole·°C; 4) alcohol; 5) aniline.

1 atm, from the data of Pizelli and Reyngart [7].

Low heat capacity in the combustion products, given equal heating yield, is a condition favorable to the creation of high specific thrust, since in this case, the major portion of the propellant thermal energy is converted into mechanical work.

TABLE 95

Efficiency Characteristics of Rocket Propellants in Terms of Maximum Speed and Range for Various Rocket Structural Factors [6-8].

1) Ракетное топливо	2) Удельный вес	3) Удельный импульс $(p/p_0 = 25)$, сек	4) Максимальная скорость (м/сек) ракеты при различных индексах конструкции ракеты			5) Максимальная дальность при $Y = 9$, км
			$Y = 1$	$Y = 2,07$	$Y = 9$	
$C_nH_{2n} + O_2$	1,0	270	1950	3000	6100	3200
$C_nH_{2n} + F_2$	1,38	290	2380	3660	6220	4020
$H_2 + O_2$	0,42	322	1090	1330	4930	1500
$C + O_2$	1,3	263	2200	3300	6270	3800
$B + O_2$	1,28	240	2020	3170	6200	3320
$Al + O_2$	1,64	207	2140	3270	5550	3350
$Si + O_2$	1,50	253	2260	3480	6050	3100
$Li + F_2$	1,0	379	2570	4270	8550	8700
$Be + F_2$	1,57	358	3320	5100	8730	9350
$B + F_2$	1,60	305	2860	4400	7500	5860
$Al + F_2$	1,76	284	2750	4260	8060	6750
$Mg + F_2$	1,60	294	2760	4220	7200	—
$Si + F_2$	1,66	260	2470	3160	7100	4230

1) Rocket propellant; 2) specific gravity; 3) specific impulse $(p/p_0 = 25)$, sec; 4) maximum speed (m/sec) of rocket for various rocket structural factors; 5) maximum range for $\gamma = 9$, km.

It should be noted that the specific thrusts given for several propellants by various sources (Tables 92, 93, and Fig. 125) are of the same order.

Table 95 gives the efficiency characteristics for rocket propellants in terms of maximum speed and range for various rocket structural factors.

In addition to the specific impulse, propellant density, which is determined by the density of its components, has a considerable effect upon rocket speed and range.
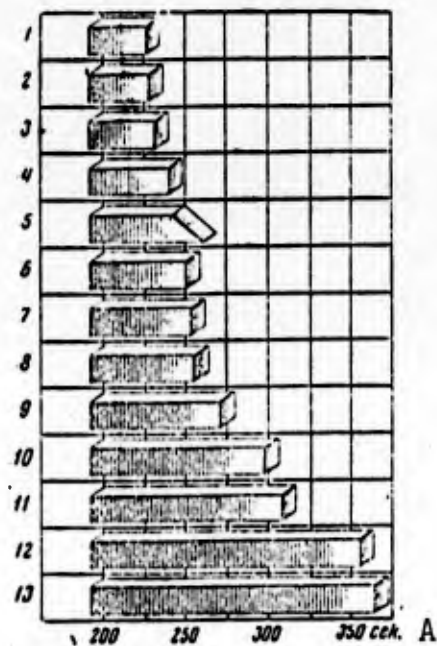
Fig. 126. Specific impulse as a function of propellant system. 1) nitric acid-aniline; 2) nitric acid-ammonia; 3) nitric acid-kerosene; 4) hydrogen peroxide-kerosene; 5) solid propellants; 6) oxygen-alcohol; 7) hydrogen peroxide-hydrazine; 8) oxygen-kerosene; 9) oxygen-hydrazine; 10) fluorine-ammonia; 11) fluorine-hydrazine; 12) oxygen-hydrogen; 13) fluorine-hydrogen. A) sec.

Thus, the density of liquid oxygen at the boiling point is 1.14, and that of liquid fluorine, 1.51. This in part accounts for the fact that fluorine is a more efficient oxidizer than oxygen.

The utilization of oxygen as an oxidizer for propellant mixtures containing Al, Mg, and even B is unfavorable in comparison with propellants based upon oxygen and hydrocarbons.

The utilization of fluorine as an oxidizer may make it desirable to use boron and beryllium [9, 10].

Since it is difficult to supply solid combustibles to ZhRD, it has been proposed that they be used in the form of suspensions in hydrocarbons or liquid inorganic compounds of boron with hydrogen (B_5H_9, $B_3N_3H_6$) and aluminum [$Al(BH_4)_3$]; this will evidently be advantageous only where fluorine is used as the oxidizer.

Of the oxidizers containing oxygen, practical utilization has been made of nitric acid, oxides of nitrogen, and hydrogen peroxide (in an auxiliary role). The possible utilization of tetranitromethane and perchloric acid has been discussed in the literature [8] (Table 96).

Figure 126 gives specific-impulse values for various reaction-engine propellants as a function of the propellant system used [13].
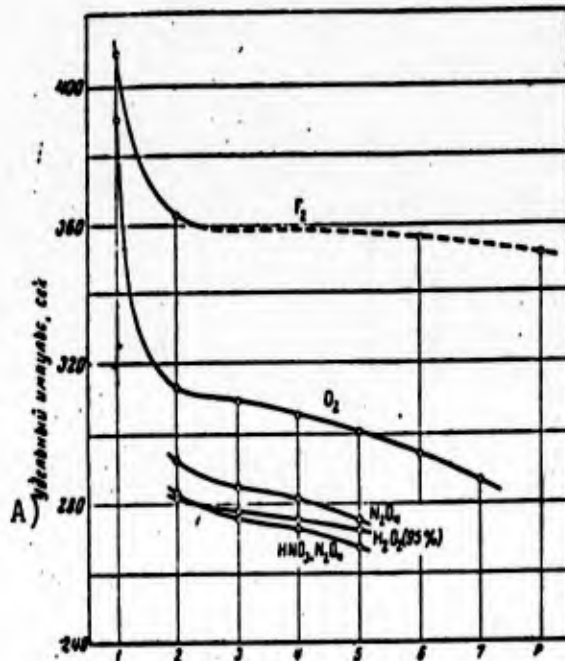
Fig. 127. Specific impulse for propellants with
various oxidizers and combustibles. Along axis of
abscissas: 1) liquid hydrogen; 2) hydrazine;
3) unsymmetric dimethylhydrazine; 4) diethylene-
triamine; 5) RP-1 kerosene; 6) ammonia; 7) ethanol;
8) diborane; A) specific impulse, sec.

TABLE 96

Characteristics for Several Rocket Propellants Using
Oxygen-Containing Oxidizers. [5, 10, 11, 12].

1) Топливо	2) Плот-ность	3) Тепло-производи-тельность, ккал/кг	4) Удельный импульс ($p/p_a=25$) сек.	5) Максимальная скорость ракеты (м/сек) при индексе конструкции		
				$\gamma = 1$	$\gamma = 2,07$	$\gamma = 9$
$C_nH_{2n} + O_2$	1,02	2270	270	1950	3020	6100
$C_2H_5OH\ (75\%) + O_2$	1,02	1760	235	1615	2100	5300
$C_nH_{2n} + HNO_3$	1,35	1450	216	1810	2840	5000
$C_nH_{2n} + N_2O_4$	1,32	1725	240	1970	3080	5440
$C_nH_{2n} + C(NO_2)_4$	1,47	1760	245	2180	3360	5840
$C_nH_{2n} + HClO_4$	1,50	1660	231	2040	3170	5500
$C_nH_{:n} + OF_2$	1,36	2530	315	2640	4140	7200

1) Propellant; 2) density; 3) heating yield, kcal/kg;
4) specific impulse (p/p_0 = 25), sec; 5) maximum
rocket speed (m/sec) for structural factor.

Figure 127 shows the specific impulse for propellants based

upon liquid oxygen and liquid fluorine, as well as other oxidizers

for various combustibles at a pressure differential p/p_0 = 67.7.

- 364 -
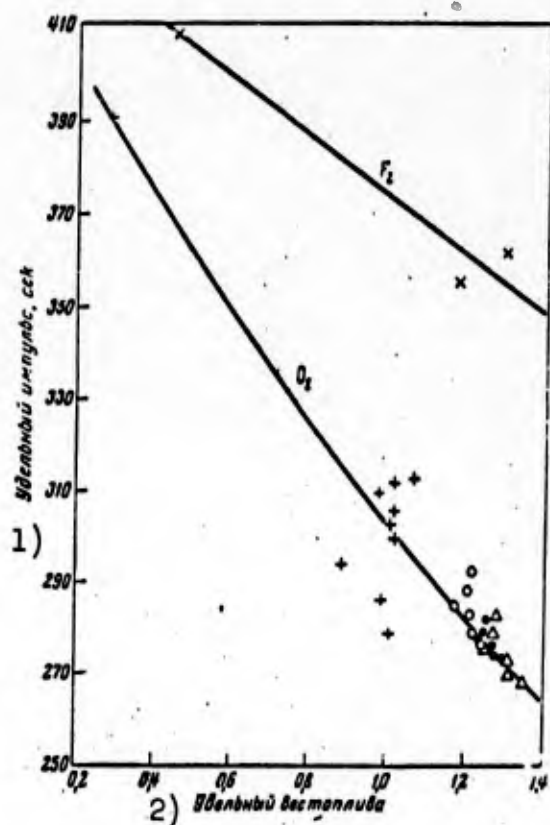
Fig. 128. Relationship between specific
impulse and density of propellants for
ZhRD. X) F_2; +) – O_2; 0) oxides of nitro-
gen-H_2O_2; △) nitric acid with oxides of
nitrogen; ●) H_2O_2. 1) Specific impulse, sec;
specific gravity of propellant.

Owing to the high density of the propellant obtained, nitric

acid has advantages in comparison with liquid oxygen for rockets hav-

ing small structural factors. It is advantageous to use liquid oxygen

for long-range purposes where the structural factors are considerable.

Figure 128 examines the relationship between specific impulse

and propellant density for a chamber pressure of 67.7 atm and a

nozzle-exit pressure of 1 atm.

Maximum specific impulse of 390-410 sec is obtained for propel-

lants having low densities in the 0.3-0.5 range, since these propel-

lants are based upon liquid hydrogen and liquid oxygen and fluorine.

The possibility of utilizing ZhRD propellants depends upon

several operating properties, of which the most important are stability and reliability of combustion, the possibility of starting the motor with the given propellants, and a secure propellant supply [14].

This entire set of factors is examined in the chapters to come for the basic forms of propellant which presently consist of propellants based upon nitric acid, oxygen, and hydrogen peroxide.

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Manu-
script   [List of Transliterated Symbols]
Page
No.

357   уд = ud = udel'nyy = specific

Chapter 3

THE ROLE OF PHYSICAL-CHEMICAL PROCESSES IN THE SELF-IGNITION, IGNITION, AND COMBUSTION OF FUELS IN ZhRD

Operating processes in liquid reaction engines are very complicated and, as yet, no theory has been developed for them. Combustion processes in engines consist of physical-mechanical phenomena, such as dispersion and mixture formation, and physical-chemical phenomena related to reaction kinetics.

We shall confine ourselves chiefly to a characterization of the physical-chemical phenomena.

1. GENERAL CONCEPTS OF THE ROLE OF PHYSICAL-CHEMICAL FACTORS IN FUEL IGNITION

Self-ignition may be considered to be a process of ignition without the participation of an open flame, i.e., at temperatures considerably lower than those developed upon combustion. In this case, the temperature corresponding to the combustion process is reached owing to reactions occurring prior to the appearance of a flame.

Autoignition is encountered in the working processes of modern internal-combustion engines. Engines using the Diesel system work on the principle of fuel self-ignition. In carburetor-type engines, on the other hand, self-ignition disturbs engine operation, and leads to knocking. In thermal-jet engines, fuel self-ignition is an advantageous phenomenon, and facilitates stable operation of the engine. In certain types of liquid reaction engines, a self-igniting fuel is

used to start the engine.

Auto-ignition may be divided into two types: "chemical" and "thermal" self-ignition.

Chemical self-ignition occurs as the result of the vigorous chemical reaction of an active oxidizer with a reactive combustible (for example, amines with nitric acid) and develops at high speed. The process is initiated at the ambient temperature (for rocket propellants, in the $\pm 40^{\circ}$ region).

Thermal self-ignition requires that heat be supplied to develop the rapidly occurring preflame reactions, and it occurs when the substance has been heated to temperatures of the order of $300\text{-}500^{\circ}$. It is observed in systems of substances with a relatively low reactivity (for example, petroleum products and nitric acids, gaseous oxygen, and hydrocarbons).

"Chemical" and "thermal" self-ignition are identical in their physical-chemical nature and differ only in the temperature region for which the ignition process is initiated.

Chemical ignition is customarily characterized by the ignition lag (or induction period), i.e., the time elapsing from the instant that the components of the reacting mixture come into contact to the time at which the flame appears.

Thermal self-ignition is characterized by the minimum temperature at which the self-ignition process develops, and also by the induction period.

A theory of self-ignition processes has been developed by N.N. Semenov, Ya.B. Zel'dovich, O.M. Todes, D.A. Frank-Kamenetskiy, et al. [1-4].

Self-ignition of a system capable of reacting endothermically (for example, as a result of oxidation reactions), may occur through

different mechanisms:

   a) thermal mechanisms;

   b) chain mechanisms;

   c) mixed chain-thermal mechanisms.

   Let us examine the essential nature of these concepts.

a) Theory of Thermal Self-Ignition

   The theory of thermal self-ignition was developed for reactions occurring in the gaseous phase, where it has received good quantitative confirmation. For auto-ignition of liquid components, where the reaction is initiated in the condensed phase, this theory can be used only for a qualitative description of the process.

   N.N. Semenov was the first to give a mathematical formulation for the self-ignition conditions: self-ignition is possible when the heat evolved from the preflame reactions is equal to or greater than the heat losses of the reacting system to the ambient medium.

   Thus, if in the gaseous phase the reaction proceeds at a rate that can be measured by the number of molecules of product appearing in one sec in unit volume, the amount of heat q_1 liberated in the entire volume v each second will be:

$$q_1 = v \frac{Q}{N} w,$$

where Q is the heat of the reaction developed upon formation of 1 g-mole of product; N is the Avogadro number; w is the reaction rate.

   The reaction rate in the initial stage will equal:

$$w = ka^n e^{-E/RT},$$

where a is the concentration of the material; n is the order of the reaction; E is the activation energy; T is the temperature; R is the gas constant.

   Then the amount of heat developed by the reaction will be

$$q_1 = v \frac{Q}{N} ka^n e^{-E/RT},$$

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or

$$q_1 = vAa^n e^{-E/RT}.$$

On the other hand, the amount of heat carried off from the reaction volume through the interface is, according to the well-known heat-transfer law, equal to:

$$q_2 = \alpha (T_1 - T_0) F,$$

where α is the heat-transfer coefficient; T_1 is the temperature of the reacting substance; T_0 is the ambient temperature; F is the heat-transfer surface.

Thus, the self-ignition conditions may be expressed mathematically as follows:

$$vAa^n e^{-E/RT} \quad > \quad \alpha (T_1 - T_0) F$$

(liberation of heat
from preflame reaction)

(loss of heat to
ambient medium)

If the reaction takes place in a spherical volume, then $v = (4/3) = r^3$ and $F = 4\pi r^2$, and we may write:

$$rA'a^n e^{-E/RT} > \alpha (T_1 - T_0).$$

When the mass of the reactant increases, the volume rises in proportion to the cube of the radius, while the heat-transfer surface increases in proportion to the square of the radius; thus, an increase in the volume of the material creates conditions favorable to the accumulation of heat.

It follows from the self-ignition conditions that system self-ignition will occur at a temperature T that is the lower the higher the initial temperature, and the higher the concentration of the reactant $\underline{a}$ of the vapor pressure P (for reactions occurring in the gaseous phase), and the greater the volume of the reactant, since the heat losses to the ambient medium will be less.

This may be illustrated by data on the way in which the ignition

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temperature of a gas-mixture combustible depends upon vessel dimensions:

Vessel volume, cm^3	Auto-ignition temperature, $^{\circ}C$
15	730
225	675

The effect of pressure upon the auto-ignition temperature of benzene vapors with air is illustrated by the following data:

Pressure, atm	Auto-ignition temperature, $^{\circ}C$
3	425
11	308
33	260

The auto-ignition temperature is related to the time given over to the selfpropagation of a preflame reaction.

Thus, for example, methyl nitrate CH_3ONO_2 at a temperature cf 269° has an ignition lag of 5 sec, and at 435°, has a lag of $1 \cdot 10^{-3}$ sec.

A similar phenomenon is observed with mixtures of hydrocarbons and air, as may be seen from the example of heptane:

Auto-ignition temperature, $^{\circ}C$	Lag, sec
680	0.003
580	0.1
540	1.0

The over-all way in which the auto-ignition temperature T depends upon the auto-ignition lag τ may be illustrated graphically (Fig. 129).

Thus, the auto-ignition temperature of a substance is not a physical constant, but depends upon experimental conditions [5]. The more time allotted for self-propagation of the preflame reactions, the lower the temperature required to initiate the process.

Despite the fact that the thermal theory of self-ignition holds,

a large number of cases are encountered in practice that do not fit within its framework.

In many cases, the induction period is connected not with heating of the mixture, but with the period of time required for isothermal selfpropagation of the reaction owing to the development and branching of chains in the reacting substance.

b) Chain Mechanism of Self-Ignition

The majority of reactions actually occurring are accompanied by a series of interconnected conversions, and thus take place in accordance with a more complicated law. The elementary stages of a complex reaction take place in accordance with the

Fig. 129. Nature of variation in self-ignition lag as a function of temperature.

laws of a mono- and bimolecular reactions, while the course of the reaction as a whole is governed by totally different relationships. It was precisely in the study of reactions not fitting within the concept of the classical course of chemical reactions that the theory of chain reactions was developed.

According to the theory of chain reactions, an excited molecule entering into a chemical reaction produces excited molecules that, reacting, in turn yield new excited molecules, etc. When an elementary reaction takes place in a medium, an energy Q is thereupon liberated, equal to the heat of reaction, and an energy E is absorbed, required for converting the molecules to the active state. This energy is initially connected with the reaction products. Later, following a series of molecular collisions, it may be transmitted to the entire volume of the reacting substance. But there may also be a case in which this energy is transmitted by collision to one or several mole-

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cules, owing to which one or several active molecules appear. Chain branching then occurs, and there may be more active molecules than would be expected from the theory of distribution of active molecules in the given gas volume in accordance with classical notions. In this case, the formation process of active molecules may proceed so vigorously that the rate of conversion of the substance rapidly reaches values corresponding to an explosion or to ignition.

c) The Mixed Chain-Thermal Self-Ignition Mechanism

In cases in which the thermal theory holds, but the induction period for self-ignition is very great, the development of chains takes place very slowly. This is explained by the fact that comparatively stable intermediate reaction products are formed, which as they accumulate react independently themselves, yielding end products. From time to time, owing to the energy of the secondary reaction, centers are created capable of again initiating a primary-reaction chain. Chain processes of these types with delayed chain branching are observed in solid and liquid explosives upon heating to comparatively low temperatures.

Investigation of the kinetics of these reactions has shown that they occur autocatalytically, i.e., the products forming as a result of the reaction accelerate the basic reaction. The change in the rate of this type of reaction with time is represented by the equation

$$W = A \cdot e \varphi^\tau,$$

where A is a certain quantity, constant for the given reaction; τ is the ignition lag time; φ is the reaction selfpropagation constant equal to $a^n e^{-E/RT}$.

If the rate of a chain reaction at some temperature that has not yet reached a certain maximum corresponding to explosion exceeds a

certain critical value W_{kr}, for which the heat of reaction will exceed the heat transferred, the thermal equilibrium will be destroyed, and in place of a chain explosion, we will observe a thermal explosion.
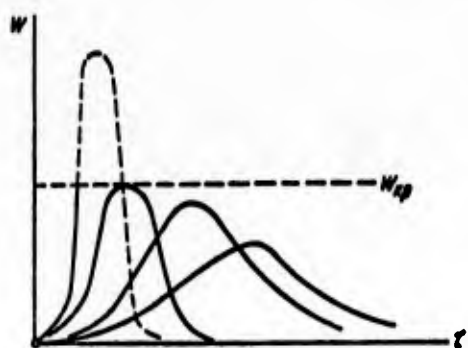
Fig. 1.30. Nature of increase in reaction rate in time τ for thermal-chain ignition.

This situation may be illustrated graphically (Fig. 130).

For cases in which the reaction rate does not reach the critical value W_{kr}, ingition and explosion will not occur.

Thus, normal ignition or explosion of a specific volume of substance occurs provided that first, specific thermal conditions and, second, specific conditions for chain development are observed.

It is clear that the more the preflame reaction is exothermal, the sooner a thermal explosion will set in and, consequently, the greater its role in the self-ignition process.

Explosives or monopropellants require a rather long period of time to become ready for self-ignition; this time is spent in the development of chains prior to the self-ignition instant. For hypergolic propellants in which an oxidizer reacts with the combustible, liberating a large amount of heat at the initial instant, slow chain development is lacking or reduced to a minimum, i.e., self-ignition occurs thermally.

2. SELF-IGNITION OF LIQUID FUELS

The process of chemical self-ignition of condensed systems begins to develop in the liquid phase and concludes in the gaseous phase, i.e., self-ignition is preceded by evaporation of the substance owing to exothermal preflame reactions that are connected with chemical con-

versions of the initial components. The fact that self-ignition is concluded in the vapor phase follows from the widely known fact that combustion always occurs in the gaseous phase [6], while self-ignition represents the initial phase of a combustion reaction.

Self-ignition of organic substances normally occurs at temperatures reaching at least several hundred degrees ($400-600^\circ$), and combustion above 1000°. At the same time, evaporation and boiling of organic combustibles and oxidizers begin at temperatures of $100-200^\circ$, while thermal dissociation commences at $300-400^\circ$. Thus, the physical process of change in the physical state of such substances begins earlier than does self-ignition.

For hypergolic rocket propellants in the liquid phase, however, preparatory exothermal preflame reactions occur. As a result of these reactions, unstable intermediate products may form, and the reacting mixture may begin heating to the boiling point of $100-200^\circ$. These reactions may limit the process as a whole.

This follows from the fact that hypergolic propellant mixtures such as nitric acid-triethylamine ignite spontaneously upon contact of the liquid components even at negative temperatures (in the sense that the development of the process commences at low temperatures), but they do not ignite in the vapor state at temperatures of $100-200^\circ$. Self-ignition of the vapors commences only at temperatures above 200°.

This phenomenon is easily explained from the point of view of thermal self-ignition. In the vapor state the density and, consequently, the concentration of the reacting substances in unit volume is several hundred times less than in a unit volume of liquid. Thus the rate of initiating reaction may be thousands of times less and, consequently, less heat is accumulated. In order to increase the
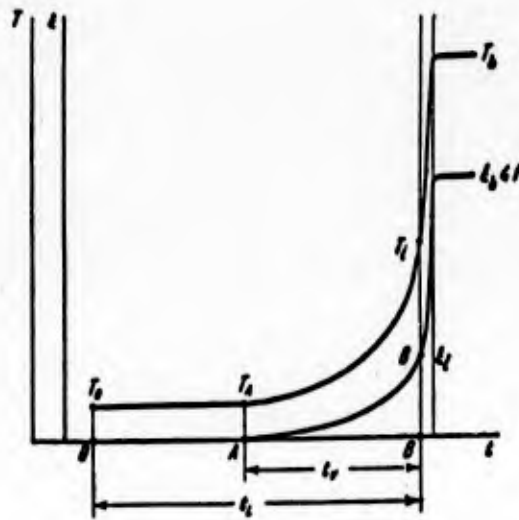
Fig. 131. Increase in temperature
and reaction rate for hypergolic
rocket propellants. (The temperature
and reaction rate are plotted on the
axis of ordinates and the reaction
time on the axis of abscissas).

reaction rate, it is necessary to raise the temperature above 200°.

The fact that unstable intermediate products are evidently formed
is also supported by the circumstance that vapors of nitric acid and
triethyl amine do not ignite spontaneously with a noticeable rate
at the boiling point, but self-ignition of these substances does occur
in vapors less than 0.02 sec after they have been mixed in the liquid
plase.

In addition to the chemical factors connected with the velocity
and exothermal nature of the preflame reactions and the physical con-
ditions that determine the heat removal, the self-ignition process
may be conditioned by physical-mechanical factors. They include all
factors that may affect the rate of mixing of the reacting components.
Among these may be numbered the viscosity and surface tension of the
oxidizer and combustible, as well as the method by which they are
mixed.

Not long ago, the following scheme was proposed for the ignition

of hypergolic rocket fuels; it takes into account the growth in the temperature of the reacting mixture and the corresponding reaction rate in time [1].

On Fig. 131, segment OA corresponds to the contact and mixing time of the propellants. In this region, the reaction is so practically imperceptible before point A, and thus the temperature T_A at point A is equivalent to the temperature T_0.

The exothermic reaction in the liquid phase begins at point A, and the temperature and reaction rate rise. Point B corresponds to the auto-ignition temperature T_i and the reaction rate W. Temperature T_b and the reaction rate W_b correspond to the beginning combustion.

The total ignition lag $\underline{t}$ is determined by the time at which the reaction begins (depending upon the rate of mixing of the components) and the auto-ignition time t_v (depending upon the rate and exothermic nature of the reaction and the heat removal).

The total time required for self-ignition depends upon chemical factors, heat-removal conditions, the physical properties of the liquid components, and the method of mixing. The role of all of these factors is not always the same. Thus, the greater the speed of the endothermal preflame reactions or, in other words, the more active the propellant, the less important the role played by the physical factors.

3. IGNITION BY OPEN FLAME

In contrast to self-ignition, which occurs at relatively low temperatures and which is associated with the accumulation of heat from preflame reactions or active centers, another mechanism is involved in the ignition of the combustible in a gas mixture in a motor by means of an open flame at a temperature of the order of 1500-3000°.

In this case, the ignition mechanism approaches the conditions observed upon establishment of a combustion process. If with self-ignition, heating of the substance as a result of the preflame reactions proceeds slowly, upon ignition by an open flame, the heat flow from neighboring layers causes a rapid increase in temperature; thus, active centers diffuse from adjacent layers.

Since ignition of liquid substances is preceded by preliminary evaporation, their ignition by an open flame amounts to heating the surface to a temperature at which rapid evaporation or boiling will occur, to mixture formation, and to ignition of the resultant vapor products.

If, however, the substance is so volatile that there is a ready-made combustible vapor-air mixture above its surface, capable of igniting, the ignition conditions reduce to those for the ignition of normal gas mixtures.

Upon injection of the oxidizer and combustible into the combustion chamber, the vaporization of individual drops represents a very slow stage in the process in comparison with the ignition of the vapors. In this case, ignition of the components by an open flame will be governed by the heat-supply and drop-heating conditions; the rate of drop heating will depend upon their dimensions.

It follows from what has been said that the degree of dispersion is of great importance; this in turn depends upon the propellant supply pressure, and upon nozzle design.

4. THE EFFECT OF THE CHEMICAL NATURE OF A PROPELLANT UPON THE OPERATING STABILITY OF LIQUID REACTION MOTORS

Pressure fluctuations (up to 50% or more) at a frequency of 10-5000 sec^{-1} may be observed upon combustion of fuel in the chambers of liquid-fuel rocket engines.

Fluctuations at a frequency of the order of 220-360 sec^{-1} are classified as low-frequency oscillations, and are accompanied by a change in pressure and radiation.

Oscillations at a frequency of 600-1500 sec^{-1} are called high-frequency oscillations [8]. They are accompanied by propagation of compression waves along the axis of the motor. These oscillations may reach such values that the motor is in danger of destruction.

The appearance of unstable pulsation combustion is observed to a large extent in low-activity diergolic propellants, where it may not appear at once, but after several seconds of motor operation. Pulsation combustion, however, can also occur with hypergolic propellants.

The appearance of pulsation combustion will disturb the supply of propellants; fuel delivery will be uneven, and will vary in time between a maximum and a minimum value, depending upon the combustion-chamber pressure fluctuations and the drop at the nozzles, which is in turn associated with the amount of propellant arriving. The magnitude of these oscillations depends upon the physical-chemical properties of the propellant and the hydraulic supply system, dispersion, and mixture formation for the propellant components.

In 1951, Summerfield [9], analyzing unstable combustion in ZhRD, advanced the idea that the appearance of oscillations upon unstable combustion is explained not only by physical-mechanical factors, but also by the existence of the induction period, i.e., a certain time interval τ between a variation in the propellant supply and the subsequent change in pressure in the chamber resulting from combustion of the propellant. The length of the induction period depends upon physical processes (dispersion, mixing, vaporization) and upon the chemical reaction of the components. With a decrease in the period of induction, the possibility of an unstable combustion regime appearing

is reduced.

The time interval from the appearance of the propellant in the motor to the formation of the end products of combustion may be represented as consisting of the following stages [10, 11]:

Atomization of the
    propellant τ_1
Heating of the
    liquid drops τ_2
Vaporization of the
    drops τ_3 } Time expended on
Heating of the sub-   physical processes
    stance to the
    temperature at
    which a reaction   } Induction
    becomes notice-   period
    able (for diergolic
    substances) τ_4 }

Reaction occurring
    with the forma-
    tion of inter-
    mediate pro
    ducts τ_5 } Time expended on
                                    chemical processes
Reaction with the
    formation of
    end products τ_6 }

A reaction accompanied by the formation of intermediate products is of great significance in the combustion process.

It determines the propellant ignition lag. The end-product formation reaction (from the instant of spontaneous ignition to conversion of the propellant into H_2O, CO_2, CO, and N_2) characterizes the combustion rate.

Thus, the induction period, depending upon the chemical processes, consists of the ignition lag τ_5 and the time required for combustion τ_6.

The quantity τ_6 is determined by the combustion rate:

$$\tau_6 \sim g\,\frac{1}{v},$$

where v is the speed of the combustion process (g/sec); g is the amount of fuel supplied in 1 sec. Thus, the induction period in the

motor is represented by the sum

$$\tau = \sum \tau_{1-4} + \tau_5 + g \cdot \frac{1}{v},$$

where $\Sigma\tau_{1-4}$ is the fraction of the induction period allotted to physical-mechanical factors.

The combustion-chamber dimensions should be such that mixing and chemical reaction can be concluded prior to arrival at the motor nozzle. The chamber dimensions necessary are determined by the value τ' for the time spent by the propellant and its combustion products in the chamber. This dwell time is found from the combustion-product volume at the combustion temperature T_k, the motor pressure P, the combustion-chamber volume V_k, the relationships PV = RT and the amount of propellant burnt in 1 sec:

$$V = g\frac{RT}{P}; \ \tau' = \frac{V_k}{V} = \frac{1}{g} \cdot \frac{V_k \cdot P}{RT},$$

where R is the gas constant; τ' is the "conversion time"; τ' is to some degree a measure of the actual time spent by the fuel and its combustion products in the chamber.

It should be kept in mind, however, that the propellant volume increases as it burns in the chamber from a very small liquid volume to a value V_k, and the dwell time is computed from this large volume.

In existing motors, the time spent in the chamber by the propellant is of the order of 0.003-0.008 sec [8]. With an increase in pressure, the time spent in the chamber rises, and thus the chamber may be smaller for the same propellant flow rate.

On the basis of a mathematical analysis, Summerfield formulated a theory according to which operating stability can be provided for the engine system of a ZhRD:

a) by increasing the pressure differential between tank and chamber;

b) by increasing the characteristic length (volume) of the combustion chamber;

c) by decreasing the cross section of ducts or increasing the mass flow rate in them;

d) by decreasing the induction period, i.e., the time from the instant of fuel injection to the creation of pressure as a result of combustion.

This last may be accomplished by an appropriate choice of propellants having a small ignition lag and a rapid combustion rate.

On the basis of the theory developed, the following equation was proposed for evaluating combustion stability parameters in ZhRD [9]:

$$\frac{l}{p_c} \cdot \frac{m}{A} + \frac{C^x \cdot L^x}{R \cdot T_c} \cdot 2 \frac{p - p_c}{p_c} > \tau,$$

where $\underline{l}$ is the length of the duct between the tank and combustion chamber; $\underline{m}$ is the propellant mass flow rate; A is the flow cross section; C^x is the characteristic velocity; T_c is the combustion temperature; $\underline{p}$ is the pressure in the tank; p_c is the pressure in the motor; τ is the induction period in the ZhRD; L^x is the characteristic length of the motor. It is the criterion determining combustion-chamber volume. L^x equals:

$$L^x = \frac{V_k}{A},$$

where V_k is the combustion-chamber volume; A is the area of the nozzle critical section. In Summerfield's opinion, the induction period in ZhRD amounts to 0.005 to 0.03 sec.

The maximum induction period should be expected for diergolic fuels — petroleum products, owing to the greater time required for evaporation in the chamber of the ZhRD, since hydrocarbons do not give a vigorous exothermal reaction with nitric acid, resulting in conver-

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sion of the components to the vapor phase.

This difference in combustion processes for nonself-igniting fuels may probably be explained in connection with the value of the initial temperature for which the fuel components begin to react.

Figure 132 shows the temperature distribution along the flame front. T_0 is the initial mixture temperature, T_v is the flash point of the material ($300-500^\circ$ for a standard determination), T_r is the initial temperature for the exothermal reaction, which is close to the combustion temperature, T_2 is the combustion temperature of $1000-2000^\circ$.

This distribution of flame temperatures was first verified by Ya.B. Zel'dovich who showed that the reaction of the matter in the flame does not begin at the ignition temperature, as had been supposed previously, but at a temperature close to the combustion temperature [3].

Fig. 132. Nature of temperature distribution T over the flame-front depth $\underline{1}$ upon combustion.
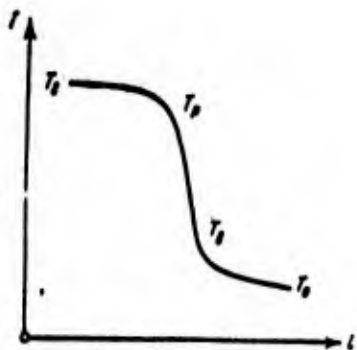
For hypergolic components, the reaction commences at a temperature close to T_0, i.e., close to the standard temperature. Thus, for hypergolic propellants, chemical interaction goes on over the entire temperature range from T_0 to T_v and T_r; the heat which develops from the preflame reaction facilitates vaporization and preparation of the propellant for combustion even prior to the supplying of heat from the combustion zone.

In addition to unstable combustion-chamber operation, motor destruction is also possible where unsuitable fuel is used. This may occur for the following reasons.

1. Upon starting, where there is an ignition lag, a large amount
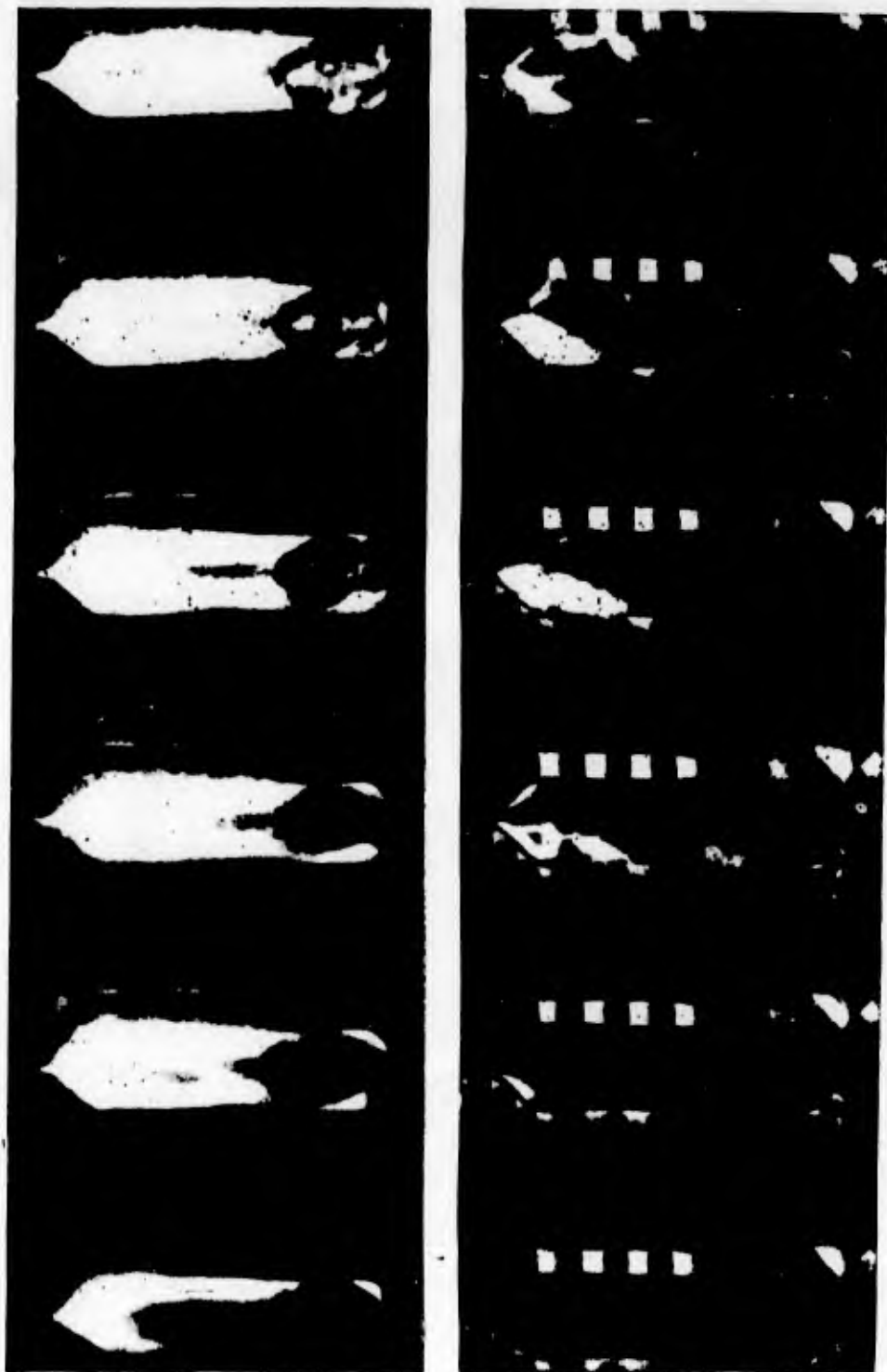
Fig. 133. Nature of ignition and combustion of nitric oxide-self-igniting combustible propellant (furfuryl alcohol-50%, xylidine-50%) in chamber of liquid reaction engine.

of fuel mixture may accumulate and as a result, at the beginning of combustion the chamber in the combustion chamber will rise above the permissible value and cause engine failure.

2. Engine destruction can also occur where the ignition lag for
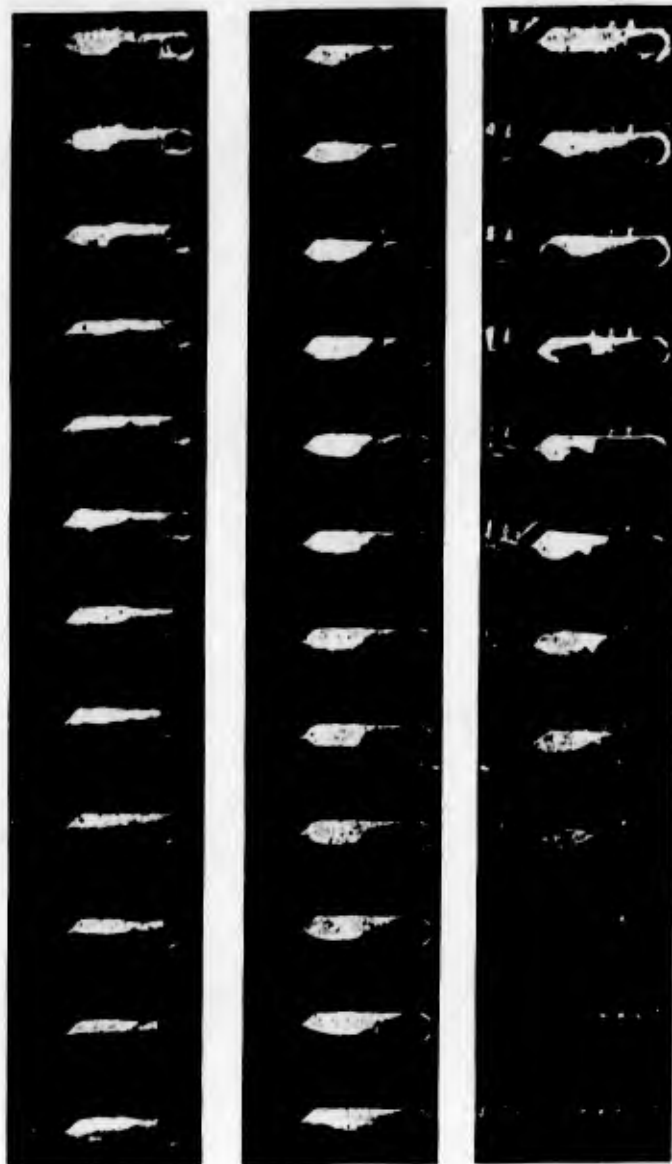
Fig. 134. Nature of ignition and combustion of fuel in liquid reaction engine.

the fuel is within normal limits, but the rate of increase in the combustion reaction from the instant of self-ignition to the establishment of steady-state conditions is too great. Thus the pressure jump in starting may exceed the pressure for which the engine was designed.

3. It is probable that combustion may transform into explosion as a result of the accumulation in the combustion chamber of a large amount of fuel mixture. As is known from practical experience, upon combustion of a large amount of explosive mixtures, there is a greater
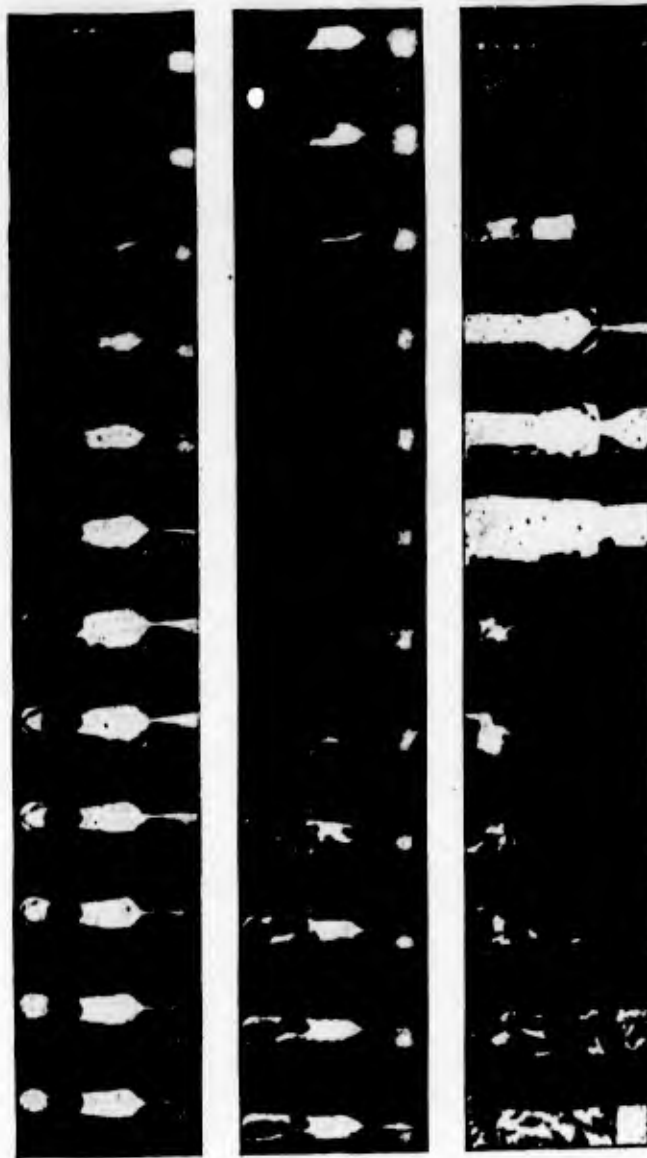
Fig. 135. Ignition of fuel, vibration combustion and explosion of ZhRD chamber after 0.1 sec.

possibility for combustion to turn into explosion since in this case, favorable conditions for the accumulation of heat are set up. Once it has begun, the combustion of such a large amount of fuel will inevitably lead to an explosion. The accumulation of relatively large masses of fuel at separate instants of time may also facilitate pulsation combustion.

4. It is also possible for "normal" combustion of a fuel mixture to turn into an explosion under operating conditions where fuels having an increased tendency to knocking are used. Transformation of com-

bustion to detonation is especially likely for liquid explosives (methyl nitrate, nitroglycerin, dinitroglycol), which were tested as monopropellants, and also for certain liquid explosive mixtures. Depending upon the nature and sensitivity of an explosive or of explosive mixtures, they will have different tendencies to go from combustion to explosion. With certain materials, successful launchings may alternate with explosions.

The explosion of a fuel mixture consisting of a finely dispersed mixture of drops of oxidizer and combustible in the liquid or mist form, is a more complicated phenomenon.

As we have mentioned, the conversion of combustion to an explosion can be described in general terms as an excess of heat arriving from the combustion zone with respect to the heat removed, from which it follows that, all other conditions being equal, conversion of combustion to explosion is more probable where large masses or volumes of materials are being burnt, i.e., in high-power motors; this has been borne out by experience.

From the heat-transfer viewpoint, steady-state combustion of a substance may be characterized by an equilibrium between the heat transfer from the combustion zone to the surface of the material and the heat expended upon evaporation of the substance.

Figures 133 and 134 show the nature of ignition and combustion of a hypergolic nitric acid-furfuryl alcohol (50%) plus xylidine (50%) propellant in the chamber of a liquid reaction engine. The process was photographed at a rate of 1680 frames per second [7].

The frames show the initiation of the propellant-ignition process in the front of the chamber, the creation of a combustion site over the entire chamber and, to the left, the creation of a flame blow-off zone at the nozzles where the propellant components are mixed and

where the reactions preceding ignition occur.

Figure 135 shows high-speed photographs of vibration combustion in a ZhRD chamber. Propellant combustion alternates with extinction and subsequent ignition over a 46-millisecond period, followed by explosion of the chamber after 96 millisec.

Thus, depending upon the conditions for the propellant-combustion process, stable combustion and unstable pulsating combustion are possible; the latter may terminate in explosion of the chamber.

Thus, both hydraulic, physical-mechanical factors, and the chemical nature of the propellant may affect operating stability of ZhRD. The chemical factor appears in the induction period and, evidently, in the tendency for normal combustion of fuel vapors to turn into reactions taking place at explosive rates. The predominating factor is determined by the arrangement of the motor and the operating regime.

Under some conditions it may turn out that the chemical nature of the propellant has no great effect upon motor operating stability, since the time involved in chemical reactions is very small in comparison with the time required for the physical-mechanical processes to take place.

It may turn out, however, upon conversion to new fuels or a rigid operating regime for the motor, that the process will be limited by the chemical properties of the propellant. In this connection, the role of the chemical nature of the propellant in combustion processes should always be kept in mind.

In general terms, these are the concepts of the ignition and combustion processes for fuels in engines. The actual process of ignition and combustion of fuels in actual engines is extremely complicated, and far from completely studied. In this chapter, we have examined

only certain considerations relating to these processes. Thus, those interested in combustion problems should turn to the specialized literature in which it is still impossible, however, to find answers to all of the questions related to processes occurring within the chambers of reaction engines [12, 13].

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Manu-script Page No.	[List of Transliterated Symbols]
375	кp= kr = kriticheskiy = critical
384	в = v = vspyshka = flash
384	p = r = reaktsiya = reaction

Chapter 4

HYPERGOLIC PROPELLANTS CONSISTING OF
SELF-IGNITING COMBUSTIBLES, NITRIC ACID,
AND OXIDES OF NITROGEN

Hypergolic propellants based upon nitric acid are classified as bipropellants, since they consist of two components: an oxidizer and a combustible, which are supplied to the motor from two separate tanks. When the oxidizer and combustible are mixed, the propellant ignites spontaneously with a very small lag, measured in the hundredths of seconds.

The advantages of hypergolic fuels (for example, nitric acid-amines) lie in the fact that no special device is required to ignite the propellant in starting the motor; they burn more stably under operating conditions than diergolic propellants (for example, nitric acid-kerosene).

Combustibles for hypergolic propellants may include aliphatic and aromatic amines, hydrazine and its alkyl-substituted derivatives, heterocyclic compounds such as, for example, furfuryl alcohol, polybasic phenols, and other substances. All of these compounds react violently with nitric acid.

It is necessary to remember that the development of the self-ignition process depends upon both chemical and physical factors.

1. Organic Compounds: Structure and Ability to Ignite Spontaneously
   with Nitric Acid

In determining the ability of organic compounds to react with nit-

- 392 -

ric acid, the first step is to make a visual evaluation of the nature of the reaction occurring when the components are mixed. For example, 1-2 ml of oxidizer and 0.5-1 ml of combustible are taken for testing. In some cases, there is no noticeable reaction, while in others there is a slow or vigorous reaction accompanied by heating and boiling. With reactive combustibles, self-ignition occurs with or without a perceptible lag.

Tables 97-99 give qualitative characteristics for self-ignition and reaction of organic compounds with 98% nitric acid and nitric acid containing 10% sulfuric acid at 20°. In chemical practice, such a mixture is called a "melange."

Thus, the following compounds ignite spontaneously with nitric acid in many cases: 1) aromatic and aliphatic amines; 2) unsaturated compounds with several unsaturated bonds; 3) polyatomic phenols; 4) certain heterocyclic compounds; 5) hydrazine and its homologs.

Primary aromatic amines ignite better with nitric acid than do secondary or tertiary amines. For aliphatic amines, the dependence is reversed, i.e., tertiary amines ignite better than secondary or tertiary [sic].

Aldehydes react relatively slowly with nitric acid.
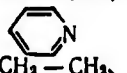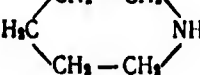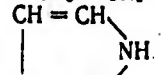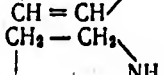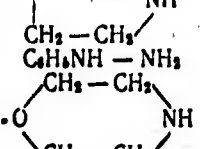
Compounds having only a single double or triple bond normally do not produce adequate ignition with nitric acid.

Compounds having two nonconjugate double bonds for the most part do not form hypergolic mixtures with nitric acid.

Conjugate double bonds increase the reactivity and liability to self-ignition. This is also facilitated by the formation of cyclic structures. Thus, pentadiene-1,4 (formula a, see below) does not have an acceptable ignition lag with nitric acid, 2-methylbutadiene-1,3 (b) does ignite, although with some lag, while cyclopentadiene (c) ignites

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TABLE 97

Interaction of Nitrogen-Containing Organic Compounds with Nitric Acid [1]

1 Соединение	2 Формула	3 Характер реакции с окислителем	
		4 98%-ная HNO₃	5 смесь 90% — HNO₃, 10% — H₂SO₄

6 Алифатические амины

	Соединение	Формула	98%-ная HNO₃	смесь
7	Диметиламин	NH(CH₃)₂	Воспламенение 19	Воспламенение 19
8	Триэтиламин	N(C₂H₅)₃	20 »	»
9	Бутиламин	C₄H₉NH₂	Реакция	Воспламенение с задержкой 22
10	Изобутиламин	18 изо-C₄H₉NH₂	19 »	Реакция 20
11	Дибутиламин	(C₄H₉)₂NH	Воспламенение	Воспламенение 19
12	Трибутиламин	(C₄H₉)₃N	20 Реакция	Реакция 20
13	Триизогексиламин	18 (изо-C₆H₁₃)₃N	21 »	»
14	β-Аминоэтиловый спирт	HOC₂H₄NH₂	Бурная реакция	Бурная реакция 21
15	Триэтаноламин	(HOC₂H₄)₃N	19 » »	То же 23
16	Этилендиамингидрат	C₂H₄(NH₂)₂·H₂O	Воспламенение	Воспламенение 19
17	Диэтилентриамин	(NH₂C₂H₄)₂NH	»	»

30 Ароматические амины

	Соединение	Формула	98%-ная HNO₃	смесь
24	Анилин	C₆H₅NH₂	19 Воспламенение	Воспламенение 19
25	Метиланилин	C₆H₅NHCH₃	21 Бурная реакция	»
26	Диметиланилин	C₆H₅N(CH₃)₂	» »	»
27	Этиланилин	C₆H₅NHC₂H₅	» »	»
28	Диэтиланилин	C₆H₅N(C₂H₅)₂	» »	»
29	Ксилидин	C₆H₃(CH₃)₂NH₂	19 Воспламенение	»

40 Гидроароматические и гетероциклические амины

	Соединение	Формула	98%-ная HNO₃	смесь
31	Циклогексиламин	C₆H₁₁NH₂	19 Воспламенение	Воспламенение 19
32	Метилциклогексиламин	C₆H₁₁NHCH₃	»	»
33	Диметилциклогексил-амин	C₆H₁₁N(CH₃)₂	»	»
34	Пиридин	[пиридин — structure]	20 Реакция	Реакция 20
35	Пиперидин	[пиперидин — structure]	19 Воспламенение	Воспламенение 19
36	Пиррол	[пиррол — structure]	»	»
37	Пирролидин	[пирролидин — structure]	»	»
38	Фенилгидразин	C₆H₅NH—NH₂	21 Бурная реакция	Бурная реакция 21
39	Морфолин	[морфолин — structure]	19 Воспламенение	Воспламенение 19

Key to Table 97

1) Compound; 2) formula; 3) nature of reaction with oxidizer; 4) 98%
HNO_3; 5) mixture; 6) aliphatic amines; 7) dimethylamine; 8) trimethyl-
amine; 9) butylamine; 10) isobutylamine; 11) dibutylamine; 12) tri-
butylamine; 13) triisohexylamine; 14) β-aminoethyl alcohol; 15) tri-
ethanolamine; 16) ethylene diamine hydrate; 17) diethylene triamine;
18) iso; 19) ignition; 20) reaction; 21) violent reaction; 22) delayed
ignition; 23) same; 24) aniline; 25) methylaniline; 26) dimethylani-
line; 27) ethylaniline; 28) diethylaniline; 29) xylidine; 30) aromatic
amines; 31) cyclohexylamine; 32) methylcyclohexylamine; 33) dimethyl-
cyclohexylamine; 34) pyridine; 35) piperidine; 36) pyrrole; 37) pyrrol-
idine; 38) phenylhydrazine; 39) morpholine.

TABLE 98

Interaction of Oxygen-Containing Organic Compounds with Nitric Acid [1]
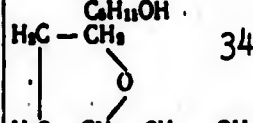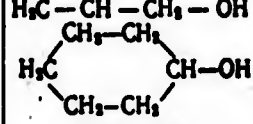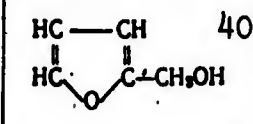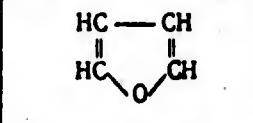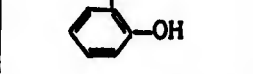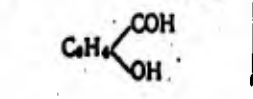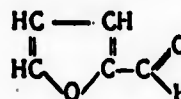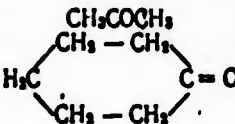
1 Соединение	2 Формула	3 Характер реакции с окислителем	
		4 98%-ная HNO₃	5 смесь 90% — HNO₃, 10% — H₂SO₄
7 Метиловый спирт	CH_3OH 30	Слабая реакция	Слабая реакция 30
8 Этиловый »	C_2H_5OH 6	То же	Бурная реакция 31
9 н. Пропиловый »	C_3H_7OH 32	Бурная реакция	То же 6
10 Изопропиловый »	изо-C_3H_7OH 33	Очень бурная реакция	Очень бурная реакция 33
11 Изобутиловый »	изо-C_4H_9OH 34	Сильная реакция	Сильная реакция 34
12 Изоамиловый »	изо-$C_5H_{11}OH$ 35	Реакция	Реакция 35
13 Амиловый »	$C_5H_{11}OH$	»	»
14 Тетрагидрофурфуриловый спирт	[структура] 34	Сильная реакция	Сильная реакция 34
15 Циклогексанол	[структура] 32	Бурная реакция	Бурная реакция 32
16 Бензиловый спирт	$C_6H_5CH_2OH$ 35	Реакция	Реакция 35
17 Аллиловый »	$CH_2 = CH - CH_2 - OH$ 33	Очень бурная реакция	Очень бурная реакция 33
18 Фурфуриловый »	[структура] 40	Хорошее воспламенение	Хорошее воспламенение 40
19 Серный эфир	$(C_2H_5)_2O$ 35	Реакция	Реакция 35
20 Этилацетат	$CH_3COOC_2H_5$ 32	»	»
21 Винилэтиловый эфир	$CH_2 = CH - O - C_2H_5$	Бурная реакция	Воспламенение с задержкой 41
22 Винилбутиловый »	$CH_2 = CH - O - C_4H_9$	То же 6	То же 6
23 Фуран	[структура] 42	Воспламенение	Воспламенение 42
24 Дикетен	$CH_2COCH = C = O$ 41	Воспламенение с задержкой	»
25 Пирокатехин	[структура] OH	—	»
26 Формальдегид (60%-ный раствор в метиловом спирте)	CH_2O 35	Реакция	Реакция 35
27 Ацетальдегид	$CH_3 - CHO$	»	»
28 Акролеин	$CH_2 = CH - CHO$	»	Воспламенение с задержкой 41
29 Салициловый альдегид	$C_6H_4(COH)(OH)$ 32	Бурная реакция	Очень бурная реакция 33

TABLE 98 (Conclusion)

1 Соединение	2 Формула	3 Характер реакции с окислителями	
		4 98%-ная HNO$_3$	5 смесь 90% — HNO$_3$, 10% — H$_2$SO$_4$
36 Коричный альдегид	C_6H_5—CH=CH—CHO	Реакция 35	Бурная реакция 32
37 Фурфурол	(furan ring with CHO)	Бурная реакция 32	Бурная реакция 32
38 Ацетон	CH_3COCH_3	Реакция 35	Реакция 35
39 Циклогексанон	(cyclohexanone ring C=O)	Бурная реакция 32	Бурная реакция 32

1) Compound; 2) formula; 3) nature of reaction with oxidizer; 4) 98% HNO$_3$; 5) mixture; 6) the same; 7) methyl alcohol; 8) ethyl alcohol; 9) n-propyl alcohol; 10) isopropyl alcohol; 11) isobutyl alcohol; 12) isoamyl alcohol; 13) amyl alcohol (pentyl alcohol; 14) tetrahydrofurfuryl alcohol; 15) cyclohexanol; 16) benzyl alcohol; 17) allyl alcohol; 18) furfuryl alcohol; 19) diethyl ether; 20) ethyl acetate; 21) vinylethyl ether; 22) vinylbutyl ether; 23) furan; 24) diketene; 25) pyrocatechin; 26) formaldehyde (60% solution in methyl alcohol); 27) acetaldehyde; 28) acrolein; 29) salicylaldehyde; 30) weak reaction; 31) same; 32) violent reaction; 33) very violent reaction; 34) strong reaction; 35) reaction; 36) cinnamaldehyde; 37) furfurol; 38) acetone; 39) cyclohexanol; 40) good ignition; 41) delayed reaction; 42) ignition.

very easily. The introduction of hetero atoms into a ring with a system of conjugate bonds, as in the case of pyrrole (d) and furane (e) does not impair the ability to ignite.

$$CH_2 = CH — CH_2 — CH = CH_2 \qquad CH_2 = CH — C = CH_2$$

(a)   b (б) CH_2

HC—CH   HC—CH   HC—CH
‖   ‖   ‖   ‖   ‖   ‖
HC CH   HC CH   HC CH
  \ /   \ /   \ /
  CH_2 NH   O

c   d   e
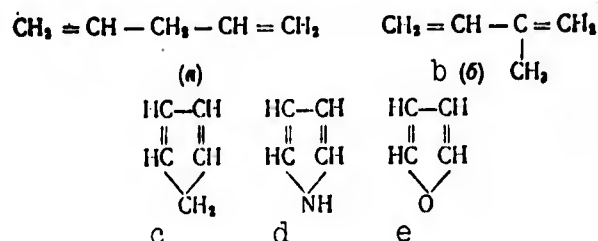
In some cases, following hydrogenation of double bonds in cyclic compounds, their ability to ignite spontaneously is preserved, and sometimes it is completely lost. This is illustrated by the data of Table 100.

TABLE 99

Interaction of Hydrocarbons and Elementary Organic Compounds with Nitric Acid [1]

A Соединение	B Формула	C Характер реакции с окислителем	
		D 98%-ная HNO₃	E 90% — HNO₃ 10% — H₂SO₄ смесь
16 Углеводороды			
1 Парафиновые углеводороды	C_nH_{2n+2}	18 Не взаимодействуют	
2 Этилен (жидкий)	C_2H_4	19 Сильная реакция	Бурная реакция 20
3 Амилен	C_5H_{10}	21 Реакция	Бурная реакция 20
4 Октилен	C_8H_{16}	20 Бурная реакция	То же 22
5 Изопрен	$CH_2=C-CH=CH_2$ / CH_3	Воспламенение с задержкой 23	Воспламенение 24
6 Циклопентадиен	$HC=CH$ ... CH_2 ... $HC=CH$	24 Воспламенение	»
7 Циклогексадиен-1,3	(cyclohexadiene ring)	»	»
8 Циклогексадиен-1,4	(cyclohexadiene ring)	21 Реакция	Реакция 21
9 Бензол	(benzene ring)	»	»
10 Мезитилен	$C_6H_3(CH_3)_3$	20 Бурная реакция	Бурная реакция 20
17 Элементоорганические соединения			
11 Этилцинк (30%-ный раствор в бензине)	$Zn(C_2H_5)_2$	23 Воспламенение с задержкой	Бурная реакция 20
12 Триэтилалюминий-эфират (10%-ный раствор в бензоле)	$(C_2H_5)_3Al \cdot O(C_2H_5)_2$	22 То же	—
13 Триэтилфосфин	$(C_2H_5)_3P$	19 Слабая реакция	—
14 Пентакарбонил железа	$Fe(CO)_5$	21 Реакция	Реакция 21
15 Тетракарбонил никеля	$Ni(CO)_4$	»	»
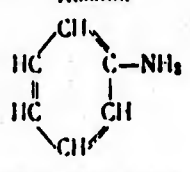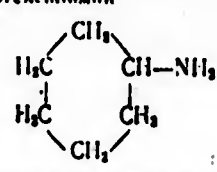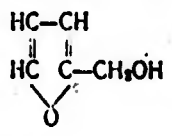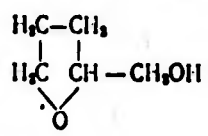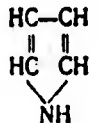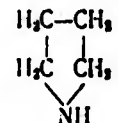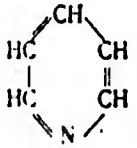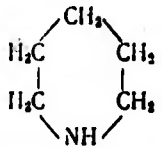
A) Compound; B) formula; C) nature of reaction with oxidizer; D) 98% HNO₃; E) mixture; 1) paraffin hydrocarbons; 2) ethylene (liquid); 3) amylene; 4) octene; 5) isoprene; 6) cyclopentadiene; 7) cyclohexadiene-1,3; 8) cyclohexadiene-1,4; 9) benzene; 10) mesitylol; 11) ethyl zinc (30% solution in benzine); 12) triethyl aluminum ether (10% solution in benzene); 13) triethyl phosphine; 14) iron pentacarbonyl; 15) nickel tetracarbonyl; 16) hydrocarbons; 17) elementary organic compounds; 18) no reaction; 19) strong reaction; 20) violent reaction; 21) reaction; 22) the same; 23) delayed ignition; 24) ignition.

Alcohols, with the exception of methyl alcohol, react violently with nitric acid. Isopropyl and allyl alcohols react the best.

In contrast to the paraffin hydrocarbons, aromatic hydrocarbons

TABLE 100

The Effect of Hydrogenation of Cyclic Compounds upon Self-Ignition with Nitric Acid [1]

1 Исходное вещество	2 Продукт гидрирования	Изменение способности к воспламенению со смесью 98%-ная азотная кислота + 4% хлорного железа 3
5 Анилин 9 Циклогексиламин 13 Немного снижается		
6 Фурфуриловый спирт 10 Тетрагидрофурфуриловый спирт Сильно снижается 4		
7 Пиррол 11 Пирролидин Сильно снижается 14		
8 Пиридин 12 Пиперидин Значительно повышается 15		

1) Starting substance; 2) hydrogenation products; 3) change in the ability to ignite with a mixture of 98% nitric acid + 4% ferric chloride; 4) decreases sharply; 5) aniline; 6) furfuryl alcohol; 7) pyrrol; 8) pyridine; 9) cyclohexylamine; 10) tetrahydrofurfuryl alcohol; 11) pyrolidine; 12) piperidine; 13) decreases slightly; 14) decreases sharply; 15) increases considerably.

such as benzene, naphthalene and their homologs react relatively violently with nitric acid, but without self-ignition.

It should be noted that multicomponent systems occasionally have greater ability to react than the individual components. Aniline mixed with cyclohexylamine, for example, ignites more easily with nitric acid than do the components taken separately.

The addition of unsaturated compounds (olefins or vinyl ethers) to amines retards the reaction with nitric acid [1]. Conversely, the

- 399 -

TABLE 101

The Effect of Amine Structure on Ignition Lag with 98% Nitric Acid [1]
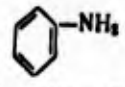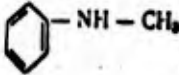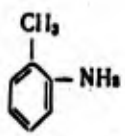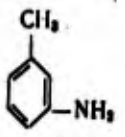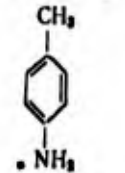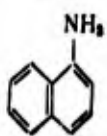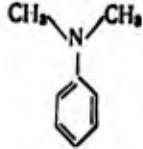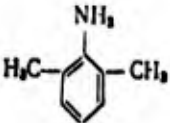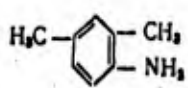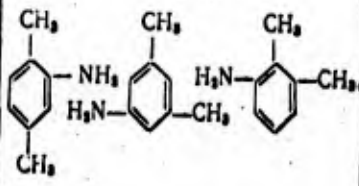
1 Название	2 Структурная формула	3 Задержка самовоспламенения, сек.
13 Первичные амины		
14 а) неразветвленные		
5 Метиламин	$CH_3 - NH_2$	Не воспламеняется (4)
6 Этиламин	$CH_3 - CH_2 - NH_2$	2,03
7 н. Пропиламин	$CH_3 - CH_2 - CH_2 - NH_2$	1,73
8 н. Бутиламин	$CH_3 - CH_2 - CH_2 - CH_2 - NH_2$	0,95
9 н. Амиламин	$CH_3-CH_2-CH_2-CH_2-CH_2-NH_2$	0,81
10 н. Гексиламин	$C_6H_{13}NH_2$	Не воспламеняется (15)
11 н. Гептиламин	$C_7H_{15}NH_2$	» »
12 н.Октиламин	$C_8H_{17}NH_2$	» »
16 б) разветвленные с аминогруппой у вторичного и третичного атомов углерода		
17 Изопропиламин	$CH_3 - \underset{\underset{CH_3}{\vert}}{CH} - NH_2$	0,94
18 Изобутиламин	$CH_3 - CH_2 - \underset{\underset{CH_3}{\vert}}{CH} - NH_2$	0,63
19 Изоамиламин	$CH_3 - CH_2 - CH_2 - \underset{\underset{CH_3}{\vert}}{CH} - NH_2$	0,57
20 Гептиламин-2	$CH_3 (CH_2)_4 \underset{\underset{CH_3}{\vert}}{CH} - NH_2$	Не воспламеняется (15)
21 Трет. Бутиламин	$CH_3 - \overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}} - NH_2$	» »
32 Вторичные амины		
22 Диэтиламин	$(C_2H_5)_2NH$	0,045
23 Ди-н. пропиламин	$(C_3H_7)_2NH$	0,17
24 Ди-н.бутиламин	$(C_4H_9)_2NH$	0,20
25 Ди-н. амиламин	$(C_5H_{11})_2NH$	0,26
26 Ди-н. гексиламин	$(C_6H_{13})_2NH$	Не воспламеняется (15)
33 Третичные амины		
27 Триэтиламин	$(C_2H_5)_3N$	0,021
28 Три-н.пропиламин	$(C_3H_7)_3N$	0,035
29 Три-н.бутиламин	$(C_4H_9)_3N$	0,24
30 Три-н.амиламин	$(C_5H_{11})_3N$	Не воспламеняется (15)
31 Три-н.гептиламин	$(C_7H_{15})_3N$	» »

Key to Table 101

1) Name of amine; 2) structural formula; 3) ignition lag, sec; 4) does not ignite; 5) methylamine; 6) ethylamine; 7) n-propylamine; 8) n-butylamine; 9) n-amylamine; 10) n-hexylamine; 11) n-heptylamine; 12) n-octylamine; 13) primary amines; 14) unbranched amines; 15) does not ignite; 16) branched amines with amino group on the secondary or tertiary carbon atom; 17) isopropylamine; 18) isobutylamine; 19) isoamylamine; 20) heptylamine-2; 21) tert. butylamine; 22) diethylamine; 23) di-n-propylamine; 24) di-n-butylamine; 25) di-n-amylamine; 26) di-n-hexylamine; 27) triethylamine; 28) tri-n-propylamine; 29) tri-n-butylamine; 30) tri-n-amylamine; 31) tri-n-heptylamine; 32) secondary amines; 33) tertiary amines.

TABLE 102
Ignition Ability of Aromatic Amines

1 Название	2 Структурная формула	3 Задержка самовоспламенения, сек.	
		4 с азотной кислотой (98%)	5 с меланжем (10 %)
6 Анилин		0,06	0,04
7 N-Метиланилин		0,12	—
8 о-Толуидин		0,15	0,06
9 м-Толуидин		0,15	0,08
10 п-Толуидин		0,15	0,00
11 α-Нафтиламин			0,06
12 N,N-Диметиланилин		>0,50	0,05
13 2,6-Диметиланилин		0,07	0,045
14 2,4-Диметиланилин		0,07	—
15 2,5-Диметиланилин		0,1	0,08
16 3,5-Диметиланилин			
17 2,3-Диметиланилин			

Key to Table 102

1) Name; 2) structural formula; 3) ignition lag, sec; 4) with nitric acid; 5) with melange; 6) aniline; 7) methylaniline; 8) o-toluidine; 9) m-toluidine; 10) p-toluidine; 11) α-naphthylamine; 12) N,N-dimethylaniline; 13) 2,6-dimethylaniline; 14) 2,4-dimethylaniline; 15) 2,5-dimethylaniline; 16) 3,5-dimethylaniline; 17) 2,3-dimethylaniline.

addition of a small amount of amines, for example aniline, to vinyl-butyl ether will increase the reaction rate.

Among the organic compounds, the most important as components of hypergolic fuels are the amino derivatives, and in this connection, amines have been subjected to very thorough studies. The ignition lag is the criterion in such investigations. Table 101 shows the effect of the position of the amines in the homolog series and their structure upon the self-ignition lag.

It is clear from the data of Table 101 that the secondary amines ignite more easily than primary amines with the same number of carbon atoms, and tertiary amines more easily than secondary.

In the homolog series of primary amines, the ability to ignite first rises and then drops as the alkyl radical increases.

The reactivity of the amine is higher with the amino group positioned at the secondary carbon atom than when it is positioned at the primary atom. This is associated with the tendency to oxidation of the corresponding amines.

Thus, among the amines having composition $C_6H_{15}N$, e.g.:

n-Hexylamine	$C_6H_{13}NH_2$.... Does not ignite	
Ethylbutylamine	$\begin{matrix} C_2H_5 \\ \diagdown \\ C_4H_9 \diagup \end{matrix}$ NH.... Ignites with difficulty	0.15-0.17 sec
Dipropylamine	$(C_3H_7)_2NH$... Ignites with difficulty	
Triethylamine	$(C_2H_5)_3N$.... Ignites easily	(0.017 sec)

only triethylamine ignites well with nitric acid, and thus it finds application in rocket propellants.

Diamines are better self-igniters than monoamines, while triamines are better than diamines as is clear from the following:

		Ignition lag, sec
Ethylamine	$C_2H_5NH_2$..............	2.0
Ethylenediamine	$H_2NC_2H_4NH_2$..........	0.09
Diethylenetriamine	$H_2NC_2H_4NHC_2H_4NH_2$....	0.01

The ability of aromatic amines to ignite spontaneously depends upon their structure (Table 102).

Of the aromatic amines, aniline and m-xylidine have acceptable ignition lags, which explains their use in recipes for hypergolic propellants in combination with other more reactive compounds.

The structure of the compound is of great importance for the aromatic amines.

Self-ignition occurs less readily with secondary aliphatic-aromatic amines than with primaries, and still less readily for the tertiary compounds, while aromatic secondary amines will not ignite spontaneously.

	Ignition lag, sec
Aniline.........................	0.06
n-methylaniline.................	0.12
n,n-dimethylaniline.............	0.5
Diphenylamine..................	Does not ignite

Consequently, we observe here a relationship that is the inverse of that for the aliphatic amine case.

The arrangement of methyl groups in the aromatic ring with respect to the amino group is of great importance.

Thus, self-ignition occurs readily for the m-xylidines. They are obtained by nitration of m-xylol with subsequent reduction of the nitro compound. In this case, only two chief isomers occur:
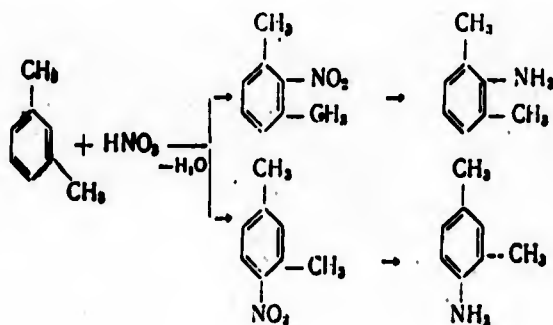
This is a technical mixture of xylidines, and is used in practice for hypergolic propellants.

Hydrazine and its simplest homologs are active self-igniting substances as vapors with 98% nitric acid.

The ignition lag for hydrazine with nitric acid is less by a factor of roughly 8-10 than that of the most active amines, and amounts to 0.003-0.004 sec.

There is an entire group of elementary organic compounds that ignite spontaneously with nitric acid; among them, the organic compounds of phosphorus have been studied (Table 103).

Ignitability has been studied in the monoalkyl phosphines RPH_2, containing up to 16 carbon atoms in the radical, in the dialkyl phosphines R_2PH, containing up to 20 carbon atoms in the radical, and in the trialkyl phosphines R_3P, containing up to 9 carbon atoms in the radical. All of these compounds ignite spontaneously upon contact with nitric acid.

In the study of the link between the chemical structure of a substance and its ability to ignite spontaneously with nitric acid, the investigations have been carried out both by pouring the reacting components into an open cup and recording the results of the reaction, and by measuring the ignition lag in special devices at atmospheric pressure or under pressure in special bombs with recording devices.

The ignition lag may depend upon the pressure at which the meas-

TABLE 103

1 Название	2 Формула	3 Температура кипения, °C	4 Задержка самовоспламенения, сек.	
			5 при +24°	5 при —40°
6 Триметилфосфин	$(CH_3)_3P$	40—42	—	0,004
7 Три-н.бутилфосфин	$(C_4H_9)_3P$	146 (50 мм)	0,0048	0,0003
8 Моно-2-этилгексил-фосфин	$C_8H_{17}PH_2$	127 (50 мм)	0,0048	0,0000
9 Моно-2-октилфосфин	$\begin{array}{c} C_6H_{13} \\ \quad\quad CH-PH_2 \\ CH_3 \end{array}$	120 (50 мм)	—	0,0085
10 Додецилфосфин	$C_{12}H_{25}PH_2$	66 (0,5 мм)	0,0050	—

1) Compound; 2) formula; 3) boiling point, $^{\circ}$C; 4) ignition lag, sec; 5) at; 6) trimethylphosphine; 7) tri-n-butylphosphine; 8) mono-2-ethylhexylphosphine; 9) mono-2-octylphosphine; 10) dodecylphosphine.

urements are made and upon the relationship of the reaction components, the combustible and the oxidizer when the reacting materials are mixed very rapidly prior to ignition.

In combustion of a propellant mixture, the maximum heat yield is given by the stoichiometric composition of components. Thus, for example:

$$(C_2H_5)_3N + 7,8\,HNO_3 \rightarrow 6CO_2 + 11,4\,H_2O + 4,4\,N_2.$$
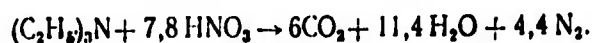
In the case of triethylamine, this relationship represents a mole fraction of combustible to oxidizer of 0.128, corresponding to $\alpha = 1$. In practice, in order to achieve maximum thrust for liquid reaction engines, α should be somewhat less than unity, i.e., 0.80-0.85. For triethylamine, this corresponds to an amine mole fraction of 0.102-0.11.

Schalla and Fletcher [2] have studied the effect of the mole relationship of combustible and oxidizer upon the self-ignition of various aliphatic amines with nitric acid (composition: HNO_3 — 97.38%, N_2O_4 — 0.6%, and H_2O — 2.02%). These investigations were carried out in a closed bomb having a volume of 430 ml into which the propellant compo-

Fig. 136. Ignition lag of tri-
alkyl amines with nitric acid
in bomb as function of mole
fraction of amine. 0) Triethyl-
amine, bomb filled with air;
●) triethylamine, bomb filled
with oxygen; Δ) tributylamine;
x) tripropylamine. 1) Ignition
lag, millisec; 2) mole frac-
tion of amine.
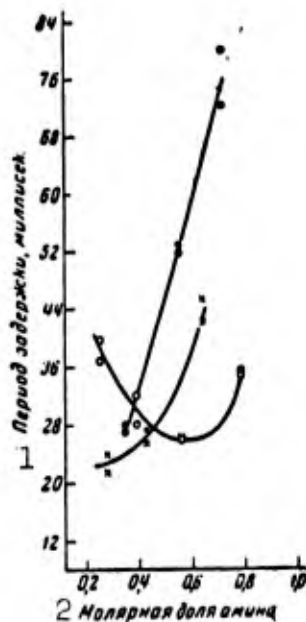
Fig. 137. Ignition lag of dial-
kyl amines with nitric acid.
0) Diethylamine; x) dipropyl-
amine; ●) di-n-butylamine. 1)
Ignition lag, millisec; 2)
mole fraction of amine.
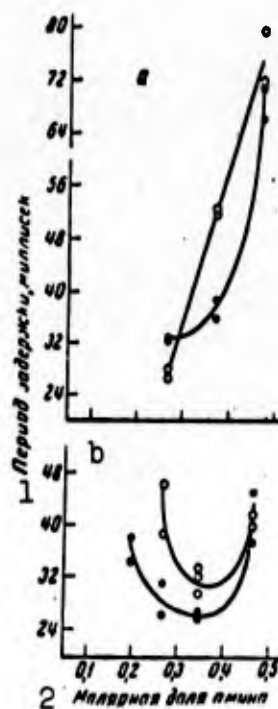
Fig. 138. Ignition lag of di-
alkyl amines with nitric acid.
a) Di-n-butylamine; b) di-n-
propylamine; ●) bomb volume,
220 ml; 0) bomb volume, 430 ml.
1) Ignition lag, millisec; 2)
mole fraction of amine.

nents were injected. Here both the change in pressure and the self-
ignition were recorded as a function of the type of amines and their
molar quantity.

The amines investigated were triethylamine, tripropylamine, tri-
butylamine, corresponding mono- and dialkyl amines.

Figure 136 shows the way in which the ignition lag varies for dif-
ferent amines —

$$(C_2H_6)_3N \quad (C_3H_7)_3N \quad (C_4H_9)_3N$$
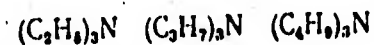
as a function of the mole fraction of the amine. The minimum ignition
lag was found where there was two or three times as much amine as re-
quired for stoichiometric composition. Here the ignition lag of tri-
ethylamine dropped by nearly a factor of three. For tripropyl- and tri-
butylamines, this excess reached a factor of five. This phenomenon is
clearly explained by the fact that the self-ignition reaction is initi-

- 409 -

ated by the heat of reaction of amine neutralization, which causes rapid heating. This heating is greatest near the mole relationship of components: 1 mole of amine to 1 mole of nitric acid. The oxygen used in some of the experiments to fill the bomb expands the ignition limits.

Naturally, triethylamine ignites with the smallest lag. The minimum ignition lag rises in accordance with the following sequence:

$$(C_2H_5)_3 N < (C_3H_5)_3 N < (C_4H_9)_3 N$$
$$0{,}004 \text{ sec} \quad 0{,}007 \text{ sec} \quad 0{,}024 \text{ sec}$$
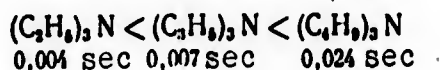
In the preflame period (2-3 millisec), the pressure in the bomb increased to 1.7-2.8 atm. Amine ignition lags in the bomb turned out to be less by roughly a factor of 4-5 than at atmospheric pressure, which may be ascribed to the elevated pressure.

Figures 137 and 138 show the way in which the ignition lag of dialkylamines depends upon the mole fraction of amine and the volume of the bomb in which the reaction takes place.

Dialkyl amines ignite spontaneously with a greater lag than trialkylamines. The law governing the relative mole relationship of the reaction components is just about the same. In a bomb of smaller volume, self-ignition occurs with a shorter lag. Monobutylamine can be made to ignite only in a bomb with rapid and good stirring.

The results given indicate that aliphatic amines ignite spontaneously with nitric acid via a stage of exothermal neutralization reaction occurring, as is the case for an ion reaction, at high speed with subsequent oxidation reactions resulting from intensive heating.

2. Effect of Catalysts upon Self-Ignition

Fuel self-ignition in a reaction engine is an oxidation reaction, and thus several inorganic salts or iron, copper, vanadium, and other metals are employed to decrease the ignition lag. All of them are oxidation catalysts.

Salts of metals with varying valence are normally used as catalysts. Here the inorganic salts are soluble in the oxidizer, and the organic salts of high-molecular organic acids in the combustible. In both cases, the agents of catalytic activity are ions of the metals.

Let us give some examples of catalytic oxidation [2].

It is known that such substances as CuO, Pd, Pt, V_2O_5, and PbO_2 in general speed up the oxidation reaction.

The catalytic action of oxides and salts of multivalent metals is explained by the ability to transport oxygen, for example:

$$2CuO + R \rightarrow RO + Cu_2O$$
$$Cu_2O + O \rightarrow 2CuO,$$
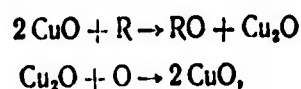
where R is an organic compound.

In many cases, a combination of several catalysts increases the catalytic effect. Thus, the mixed catalysts $CuO + Cr_2O_3$ and $MnO_2 + PbO_2$ are known; they have greater activity than the oxides taken separately.

Oxidation catalysts find wide application in technology. Thus, the catalyst "hopcalite" having the composition $MnO_2 - 50\%$, $CuO - 30\%$, $Cr_2O_3 - 15\%$, $Ag_2O - 5\%$ is used in the oxidation of carbon monoxide by atmospheric oxygen at normal temperatures.

The process of oxidizing carbon monoxide into carbon dioxide by means of the oxygen of the air in the presence of hopcalite is used in filtering gas masks designed for protection against carbon monoxide.

To intensify surface combustion in gas torches, catalysts of the following composition are used: $ThO_2 - 99\%$, $CeO_2 - 1\%$ and a mixture of oxides of MnO_2 and Al_2O_3 with 6-18% added Cr_2O_3.

Catalysts containing Cu and Ag are used to oxidize methane to formaldehyde.

Self-oxidation of unsaturated compounds such as the terpenes is accelerated by rosin and naphthenic salts of Co, Fe, Mn, Cr, Os, and Pb.

When dissolved in turpentine, these salts sometimes cause the turpentine to ignite spontaneously with the air.

TABLE 104

Some Catalysts used in Hypergolic Propellants
[1, 3, 4]

1 Катализатор	2 Формула	3 Топливо	4 Куда вводится катализатор	
6 Хлорное железо	$FeCl_3 \cdot 6H_2O$	Азотная кислота, амины, непредельные 14	В окислитель	5
7 Нитрат железа	$Fe(NO_3)_3$	То же 15	В окислитель	22
8 Железная соль дибутилнафталинсульфокислоты	$[(C_4H_9)_2C_{10}H_5SO_3]_2Fe$	Перекись водорода, пирокатехин, растворители 16	В горючее	23
9 Соли органических кислот	$(RCOO)_{2-3}Me$	Азотная кислота, амины, непредельные 17	В горючее	23
10 Медносинеродистый калий	$K_2Cu(CN)_4$	Перекись водорода, гидразингидрат, метиловый спирт 18	В горючее	23
11 Окислы и соли меди	CuO Cu_2Cl_2	Азотная кислота, непредельные, перекись водорода 19	В окислитель	22
12 Соединение ванадия	$V_2O_2Cl_4 \cdot 5H_2O$	Перекись водорода, горючее 20	В горючее	23
13 Соединения марганца (перманганаты)	$KMnO_4$ $NaMnO_4$ $Ca(MnO_4)_2$	Перекись водорода, горючее 21	Впрыскивается в двигатель	24

1) Catalyst; 2) formula; 3) propellant; 4) where catalyst is introduced; 5) in oxidizer; 6) ferric chloride; 7) ferric nitrate; 8) iron salt of dibutyl naphthalene sulfonic acid; 9) salts of organic acids; 10) potassium cupricyanide; 11) oxides and salts of copper; 12) compound of vanadium; compounds of manganese (permanganates); 14) nitric acid, amines, unsaturated; 15) same; 16) hydrogen peroxide, pyrocatechol, solvents; 17) nitric acid, amines, unsaturated; 18) hydrogen peroxide, hydrazine hydrate, methyl alcohol; 19) nitric acid, unsaturated, hydrogen peroxide; 20) hydrogen peroxide, combustible; 21) hydrogen peroxide, combustible; 22) in the oxidizer; 23) in the combustible; 24) injected into the engine.

The activity of a catalyst is graphically characterized by the amount of heat liberated in 1 hr upon oxidation of the paraffins of petroleum jelly:

	Heat of reaction, kcal/hr
Manganese stearate.............	31
Manganese palmitate...........	45
Copper naphthenate............	106
Manganese naphthenate.........	198
Cobalt naphthenate............	234

In this reaction, the salts of cobalt are more active than those of manganese or copper, and in their presence, oxidation proceeds at the greatest rate.

There is a maximum amount of catalyst exceeding of which will produce no further increase in the reaction rate. Thus, the heat yield from the oxidation of petrolatum with manganese naphthenate increases only to a concentration of 0.8%, following which the reaction rate does not rise.

It has been noted that in the oxidation of petroleum fractions, a combination of metals may prove to be a more active catalyst than salts of the metals taken separately.

All of the laws given may be considered in choosing ignition catalysts for reaction fuels.

Table 104 lists the substances finding application as ignition catalysts in reaction fuels.

The catalysts to some degree act selectively with respect to the various combustibles and oxidizers. Thus, such unsaturated compounds as aromatic amines are sensitive to the action of catalysts when igniting spontaneously with nitric acid. At the same time, aliphatic amines are quite insensitive to catalysts.

Where nitric acid with an admixture of sulfur is employed, i.e., "melange," catalysts have less effect upon the ignition lag than where pure nitric acid is used. The addition of sulfuric acid to the nitric

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acid decreases the ignition lag for amines and unsaturated compounds.

In the first case, sulfuric acid, being more aggressive, increases the heat yield of salt formation while in the second case the sulfuric acid evidently acts as a catalyst: the sulfuric acid increases the reaction rates of nitration and polymerization, which may facilitate the development of preflame oxidation reactions owing to the exothermal effect.

3. On the Mechanism of Spontaneous Ignition of Organic Combustibles and Nitric Acid

Spontaneous ignition of organic combustibles upon contact with oxidizers is preceded by several intermediate reactions which commence under normal conditions and proceed at high speed. The initial vigorous heating of the reaction mixture initiates the subsequent preflame oxidation reactions that then lead to self-ignition.

Thus it may be expected that triethylamine with nitric acid will form a nitrate accompanied by the evolution of a considerable amount of heat:

$$(C_2H_5)_3N + HNO_3 \rightarrow (C_2H_5)_3N \cdot HNO_3 + 27,6 \text{ kcal.}$$
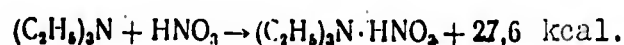
The reaction between a strong acid and a base is of an ionic nature, and proceeds at high speed; as a result, the heat developed cannot be dissipated. This in turn leads to heating of the reaction mixture and to oxidation of the entire molecule.

Upon interaction of aniline with nitric acid and oxides of nitrogen, the following reactions may develop in the initial stage [4], in connection with the evolution of heat:

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$$NH_2 \cdot HNO_3 \quad +19,0 \text{ kcal}$$

$$\text{(aniline)} + HNO_3 \rightarrow \begin{cases} NH_2 \cdot HNO_3 \\ NH_2, N_2O_5 \\ NH_2 \text{-}NO_2 \quad +17,0 \text{ kcal} \\ NO_2 \\ N_2 \cdot NO_3 + \dfrac{42 \text{ kcal}}{H_2O} \rightarrow OH \xrightarrow{HNO_3} OH\text{-}NO_2 \end{cases}$$
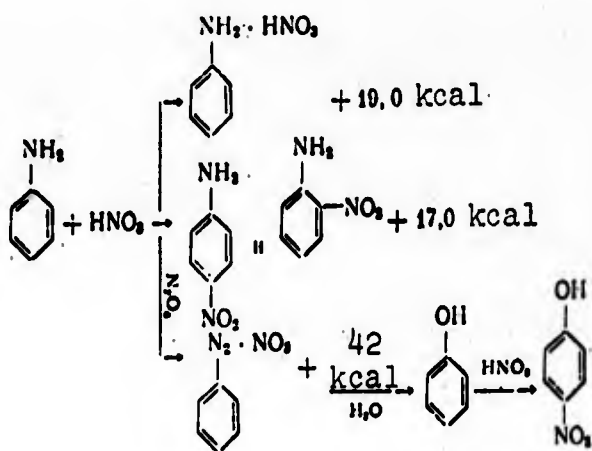
The possibility of such reactions is well known in organic chemistry [4], and the question lies in the degree to which they actually occur.

In a hypergolic reaction of a hydrocarbon — pentadiene — with nitric acid, the following reactions may be supposed to occur in the initial state [5]: 1) the attachment of nitric acid at the double bond with the formation of a nitroalcohol; 2) addition with the formation of a nitroether, and 3) polymerization of the two pentadiene molecules under the action of the acid:

$$HC\text{-}CH, HC\text{-}CH, CH_3 + HNO_3 \rightarrow \begin{cases} \text{nitroalcohol} \quad +20,3 \text{ kcal} \\ \text{nitroether} \quad +12 \text{ kcal} \\ \text{dimer} \quad +24 \text{ kcal} \end{cases}$$
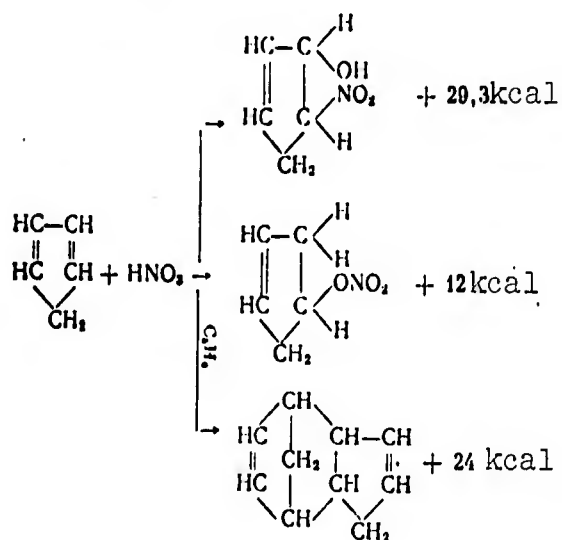
For the monoolefins, such as cyclohexene, all three reactions may occur, although at a considerably lower rate. Thus, the reaction mixture will be cooled owing to heat transfer, and self-ignition will not occur.

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TABLE 105

Heat of Reaction and Nominal Heating of Amines and
Unsaturated Compounds with Nitric Acid [6]

1 Реакция	2 Теплота реакции, ккал/моль	3 Условный разогрев, °C	4 Период задержки самовоспламенения с азотной кислотой, сек.
$C_6H_5NH_2 + HNO_3 \rightarrow C_6H_5NH_2 \cdot HNO_3$	19	247	0,06
$C_6H_5NH_2 \cdot HNO_3 + HNO_3 \rightarrow C_6H_5N_2NO_3 + 2H_2O$	23	—	—
$C_6H_5NH_2 + HNO_3 \rightarrow C_6H_4\langle{}^{NH_2}_{NO_2} + H_2O$	17	218	0,06
$(C_2H_5)_3N + HNO_3 \rightarrow (C_2H_5)_3N \cdot HNO_3$	27,6	336	0,02
$(C_5H_{11})_3N + HNO_3 \rightarrow (C_5H_{11})_3N \cdot HNO_3$	27,6	170	1
$C_6H_6 + HNO_3 \rightarrow C_6H_6\langle{}^{H}_{ONO_2}$	+12	180	—
$C_6H_6 + HNO_3 \rightarrow C_6H_6\langle{}^{OH}_{NO_2}$	20,3	440	0,03
$C_6H_6 + C_6H_6 \rightarrow (C_6H_6)_2$	+24	230	-

1) Reaction; 2) heat of reaction, kcal/mole; 3)
nominal heating, °C; 4) ignition lag with nitric
acid, sec.

Table 105 gives data for the nominal heating of a reaction mix-
ture which might be obtained where there are no side reactions and no
heat expended upon vapor formation. In this case, the heating is de-
termined by the relationship

$$t = \frac{Q \cdot 1000}{C_p \cdot M},$$

where Q is the heat of reaction; C_p is the heat capacity of the reac-
tion mixture, equal to roughly 0.5 cal/g; M is the total molecular
weight of the reacting components.

In actuality, heating of the reaction mixture also occurs owing
to the oxidation reactions that develop when the temperature rises in
the nitric acid.

The special role of the amino groups in the self-ignition reac-
tion of aromatic amines with concentrated nitric acid is clearly in-
dicated by the fact that other light oxidizing substances (phenols,
naphthols, hydroquinone, pyrocatechol) do not directly ignite spon-

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taneously with nitric acid.

As the molecular weight rises, the tendency to self-ignition in the homologous group of amines decreases. At the same time, owing to the increase in molecular weight, there is a drop in the temperature to which the reaction mixture is heated due to the formation of nitrate. Thus, for triethylamine, the nominal temperature of heating with nitric acid amounts to 336°, while for triamylamine, it is only 170°. The structure of the amine is also of considerable importance, however. Thus, triethylamine $(C_2H_5)_3N$ ignites easily, while hexylamine $C_6H_{13}NH_2$, an isomer of triethylamine, does not ignite with nitric acid within an acceptable lag period. It is possible that this is connected with the basicity of amines, which is higher for the tertiary amines than for the primary. The relationship works the other way for aromatic amines, i.e., the primary amines are more active in a self-ignition reaction than the tertiary amines. This is supported by the fact that the mechanism for self-ignition of aromatic amines differs from that for aliphatic amines.

The aliphatic and aromatic amines also differ in basicity. Thus, the dissociation constant of aniline as a base is $4.6 \cdot 10^{-10}$, and that of triethylamine is $6.4 \cdot 10^{-4}$, i.e., the basicity of triethylamine is far greater.

When nitric acid is reacted with unsaturated hydrocarbons, in the first stage it is possible to obtain easily oxidized nitroethers and nitroalcohols which can oxidize further as a result of heating.

Trent and Zucrow [7] attempted to study the self-ignition mechanism of dicyclopentadiene with nitric acid; they isolated intermediate products of a delayed reaction between these reagents.

Dicyclopentadiene ignites spontaneously when mixed with 1-2 ml of nitric acid, but if 90% HNO_3 is added carefully in very small portions,

drop-wise, to this hydrocarbon, it is possible to avoid spontaneous ignition. In this case, there is an exothermic reaction resulting in the separation of an amorphous dark-red precipitate which may be isolated and studied. When this substance is heated to 160-200°, an explosion results; with the addition of several drops of nitric acid, the explosion commences as low as 100°. The same reaction may be produced in a solution of CCl_4.

When dicyclopentadiene and nitric acid are reacted in a solution of carbon tetrachloride, solid substances, representing products of the reaction between $C_{10}H_{12}$ and HNO_3 were separated. Their properties are shown in Table 106.

TABLE 106

Composition of Reaction Products for Nitric Acid and Dicyclopentadiene

1 Взято реагентов, г		2 Молярное отношение $C_{10}H_{12}$: HNO_3	3 Образовалось твердого вещества, г	4 Элементарный состав, %				5 Температура разложения (вспышка), °C
$C_{10}H_{12}$	HNO_3			C	H	N	O	
13,2	6,3	11	3,8	53,79	4,69	8,19	33,33	155—160
13,2	12,6	12	9,6	51,80	4,73	9,05	34,42	172
13,2	18,3	—	10,4	51,62	4,85	8,98	—	200

1) Reagents taken, g; 2) mole proportion; 3) solids formed, g; 4) elementary composition; 5) dissociation (flash) point, °C.

These substances clearly contain a nitroether group and a nitro group. They most likely represent high nitrated polymers of dicyclopentadiene, since the latter is easily polymerized under the action of nitric acid.

Experiments designed to obtain reaction products for nitric acid and dicyclopentadiene were carried out in a 250-ml glass flask in which were placed 0.1 mole of dicyclopentadiene in a solution of 60 ml of carbon tetrachloride. 0.1 or 0.2 mole of 99% nitric acid was added to the solution drop-by-drop.

High-speed photography (at a rate of 1500 frames per second) of the self-ignition process in dicyclopentane upon mixing with nitric acid showed that even after 0.002 sec, the formation of a solid phase could be observed. The initial ignition of the vapors above the liquid phase was observed after 0.005 sec, while the main ignition reaction developed in 0.025-0.03 sec.

High-speed photography of the self-ignition process in other fuels in all cases revealed an initial violent boiling of the mixture, followed by the appearance of isolated ignition sites in the vapors which combined to form a flame.

The addition of sulfuric acid to the nitric acid facilitates the development of polymerization reactions, and for amines favors salt formation and acid catalysis in general, since sulfuric acid is stronger than nitric acid. Thus, the addition of 10-20% of concentrated sulfuric acid to nitric acid promotes ignition and decreases the ignition lag.

4. Method of Investigating Hypergolic Propellants

One of the important parameters of hypergolic propellants is the ignition lag, measured from the instant of contact of the oxidizer with the combustible to the appearance of the flame. The ignition lag should not exceed 0.03 sec. The shorter the time elapsing between the start of fuel-component supply to ignition, the lower will be the mass of propellant stored in the motor, the less the pressure developed at the instant of propellant ignition, and the easier the start.

Electronic equipment is used to determine the ignition lag of propellant components (oxidizer and combustible) upon contact. Under laboratory conditions, two basic methods are used to determine ignition lag:

1) combining the two propellant components in the vessel of a mix-
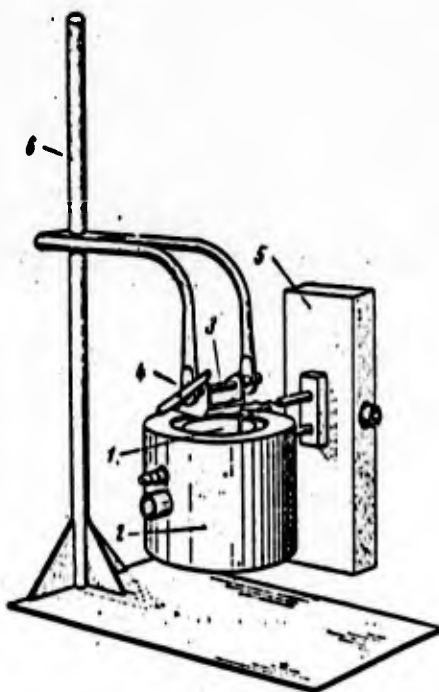
Fig. 139. General view of installation for determining induction period. 1) Vessel with oxidizer; 2) thermostat; 3) vessel with combustible; 4) rotating mechanism; 5) pulse generator; 6) support.
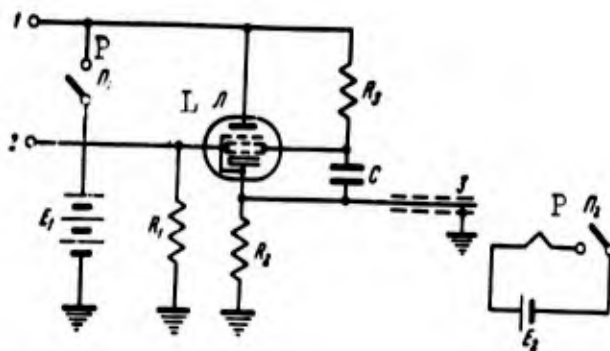
Fig. 140. Circuit of pulse generator of recording installation for determining ignition lag. 1) To vessel with combustible; 2) to vessel with oxidizer; 3) to sweep generator. R_1) 1 Meg; R_2) 25,000 ohms; R_3) 100,000 ohms; C) 0.001 μf; L) tube; E_1) 67.5 v (DC); E_2) 1.5 v (DC); P_1 and P_2) switches (normally open).

ing- or drop-type instrument;

2) causing contact of jets issuing from a special nozzle in a jet instrument.

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The recording equipment may be quite varied.

Figure 139 shows a general view of an installation for determining ignition lag for hypergolic propellants in a mixing-type instrument [8] using an electronic timer. A specific quantity of oxidizer is poured into the cast glass vessel 1, located in thermostat 2 at the required temperature. The combustible is in vessel 3, which is connected to a rotating mechanism. Upon rotation, the combustible is poured from the vessel into the oxidizer, following which self-ignition occurs.

The ignition lag is assumed to be the time elapsing between the touching of the oxidizer surface by the combustible and the appearance of the flame.

The timing equipment includes a pulse generator, cathode-ray oscilloscope, and a photocell with amplifier and signal generator.

Figure 140 shows the pulse-generator circuit. At the instant the combustible makes contact with the oxidizer, a positive charge appears upon the control grid (the cathode is connected to a contact touching the oxidizer, and the anode to the combustible); as a result, there is a certain voltage jump. This pulse is applied to the sweep generator and then to the oscilloscope, whose screen shows a horizontal trace. The photocell and amplifier register the instant of appearance of the light due to the reaction; this causes a vertical deflection of the cathode-ray beam. The length of the trace from the initial point to the first vertical deflection is a measure of the induction period. The oscilloscope screen is photographed continuously with the aid of a special photographic attachment.

Figure 141 shows a typical oscillogram for a propellant consisting of fuming nitric acid and a mixture of furfuryl alcohol (80%) and aniline (20%). The frequency of the signal voltage is 200 cps, and thus

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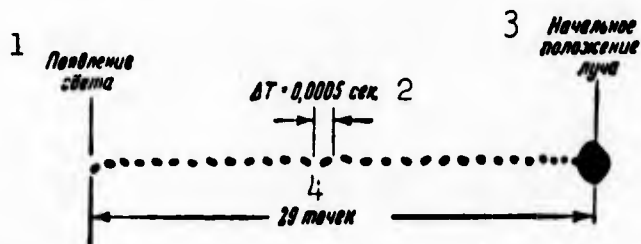
Fig. 141. Oscillogram obtained in deter-
mination of the self-ignition period of
a nitric acid-furfuryl alcohol and ani-
line propellant at temperature of 20°
(induction period, $0.005 \cdot 29 = 0.0145$ sec).
1) Appearance of light; 2) sec; 3) ini-
tial beam position; 4) points.
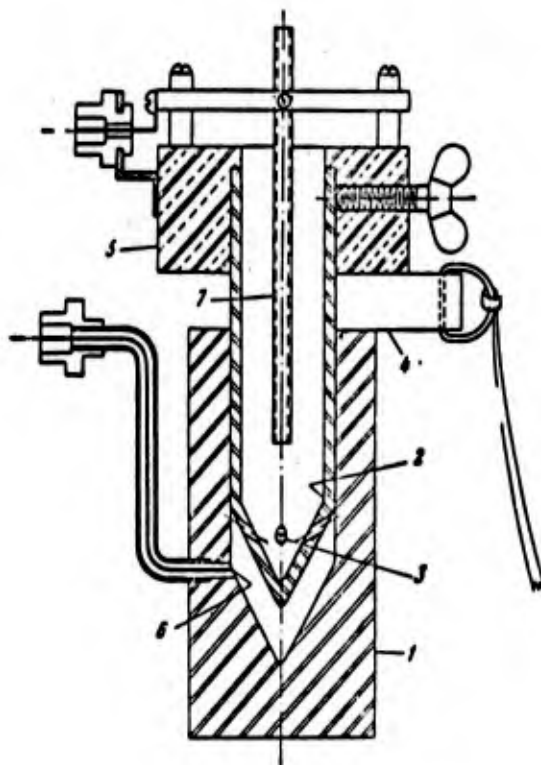
Fig. 142. Diagram of transducer for de-
termining ignition lag. 1) Cylinder for
oxidizer; 2) cylinder for combustible;
3) openings; 4) weight holder; 5) weight;
6 and 7) electrodes transmitting pulse.

the distance between the separate points corresponds to 0.5 millisec.

Consequently, the 29 markers of the oscillogram correspond to an induc-

tion period of 14.5 millisec, or 0.0145 sec. 8-10 determinations are

carried out in order to obtain an average result.

Figure 142 shows the arrangement of a new design for a mixer-type

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transducer. The details of this device were published in 1955 [9].

The outer cylinder contains 3 ml of oxidizer, and the inner cylinder, 1 ml of combustible. In order to determine the ignition lag, the supporting block is removed, and the inner concentric cylinder with the combustible is forced by the weight to drop into the outer cylinder. As a result, the oxidizer and combustible are mixed through the openings in the inner cylinder, and ignition then occurs. At the instant of propellant contact, the first pulse is sent out by electrode 6, while the second pulse is sent through electrode 7 owing to the ionizing effect of the flame.

Rocket-propellant ignition-lag determinations are made in an exhaust hood, since oxides of nitrogen and nitric acid vapors are released upon ignition of the propellant. Careful precautions must be taken to prevent spattering of acid and burning propellant particles, especially since in some cases propellant ignition may be explosive in nature.

In the drop-type instrument [10], one of the propellant components (the combustible) is added by means of a special dropper to the second component, located in a small quartz crucible (Fig. 143). Along the way, the drops intercept a light beam that falls upon a photorecording camera. Flashing of the mixture is recorded by a second camera with the aid of a photocell. The ignition lag is found from the photographic data.

With the aid of a capacitor-type pressure transducer and associated equipment, the device makes it possible to record the change in pressure in a special chamber to which the propellant components are supplied during the period between mixing and ignition.

High-speed photography may be used to find the ignition lag in a drop-type instrument.
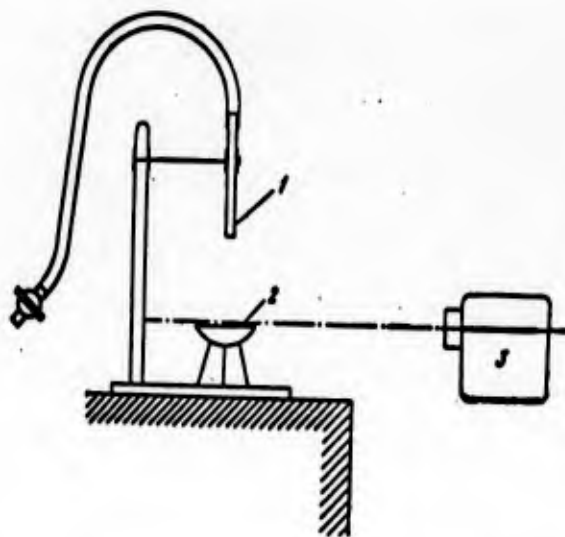
Fig. 143. Diagram of drop-type instrument
for determining ignition lag. 1) Nitric
acid; 2) self-igniting combustible; 3)
high-speed camera.
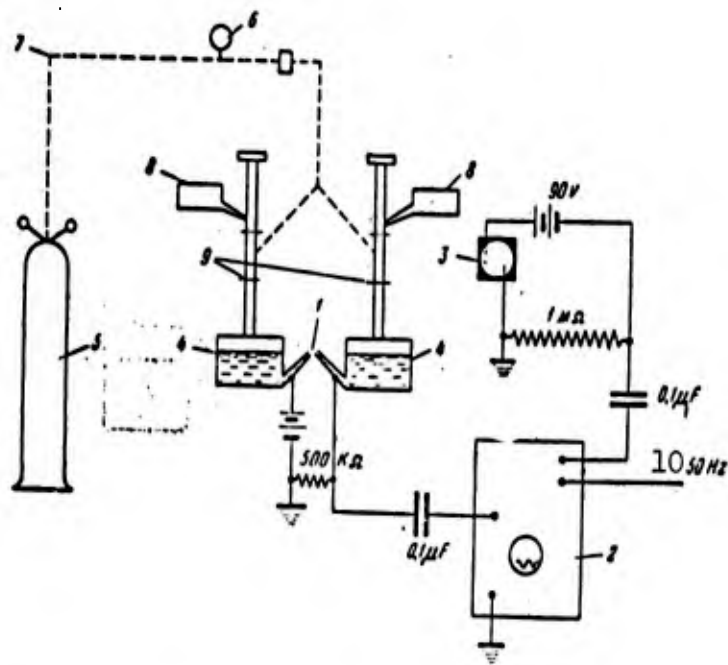
Fig. 144. Diagram of jet-instrument arrangement for
determining lag in hypergolic fuels. 1) Jets of
oxidizer and combustible; 2) electrical sensor re-
cording contact of jets and pulse photocell; 3)
photocell; 4) cylinders with oxidizer and combus-
tible; 5) cylinder with compressed air; 6) pres-
sure gauge; 7) compressor line; 8) additional cyl-
inders with propellant components; 9) solenoid
valve; 10) 50 cps.

High-speed photography has shown that when the propellant compo-

nents are mixed, violent boiling of the mixture occurs followed by ig-

nition and propagation of the flame from the ignition sites, which appear in isolated points of the vapor cloud.

Drop-type instruments have evidently not found wide application.

The use of jet devices [10] to determine ignition lag is quite interesting, since the mixing of the propellant components occurs in jets, which permits the experiment to be set up under conditions approaching those of a motor. The use of a jet device makes it possible to obtain more accurate results than are possible with a drop-type instrument. In the jet-type instrument, the two intersecting oxidizer and combustible streams, which flow out from capillaries, form a complex stream at their intersection with ignition occurring on some section of the complex stream. The length of the composite stream is proportional to the ignition lag. The ignition lag is determined with the aid of a recording instrument in terms of the time elapsing from the instant the streams combine to their ignition.

In order to form the combined stream, each of the capillaries serving to supply the propellant components may be raised and lowered. In addition, the angle between them may be varied over a 15 to 100° range. The capillaries are located in the vertical direction by clamping each of them to a special coupling that slides along two guide rods. In order to fix the capillaries at the precisely specified angle to each other, the guide rods are fastened to arms. One end of each arm is fastened along a common axis on one side of the instrument. The other end of each arm slides along a graduated scale, and may be locked to it at any angle.

The propellant components are kept in special cylinders connected with the capillaries by means of vinyl chloride tubes. The propellant is supplied with the aid of compressed air at 0.4-0.6 atm (gauge). The compressed air is supplied from constant-pressure 20-liter cylinders.

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The gauge pressure is reduced with the aid of a solenoid escape valve, and is recorded by means of a mercury manometer. The pressure is also automatically raised to the required limit. There is a permanent electrical contact in the manometer column, installed at a predetermined pressure used in the electrical system to maintain the pressure automatically (Fig. 144).

The instrument is actuated when compressed air is supplied through solenoid valves to the pressure line leading to the propellant tanks.

The propellant-component flow rate is regulated by varying the diameter or length of the capillaries, and also by changing the supply pressure. The capillaries used were 0.5 in diameter and 180 mm long. In this case, with a pressure of 0.9 atm (gauge) the supply of liquid amounted to 1 g/sec. The flow rate of each propellant component was determined in a separate experiment by supplying liquid to a graduated cylinder for a specified time interval.

The instrument can be controlled remotely; control centers in a small distribution panel upon which there are three switches and a signal lamp. The main switch controls both supply lines, while the other two control the supplies of combustible and oxidizer. The signal lamp indicates that the main switch is closed.

Preparation for measurements amounts to establishing the flow rate and choosing the required height for the capillary output holes in order to achieve complete mixing of the streams.

High-speed photography of the ignition process has established that boiling of the liquid fuel in the jet precedes ignition. The propellant vapors then ignite and the flame propagates along the jet to the point at which the components merge into the common stream.

Figure 145 is a photograph of a jet device in action.

In addition to the standard instruments, special small laboratory
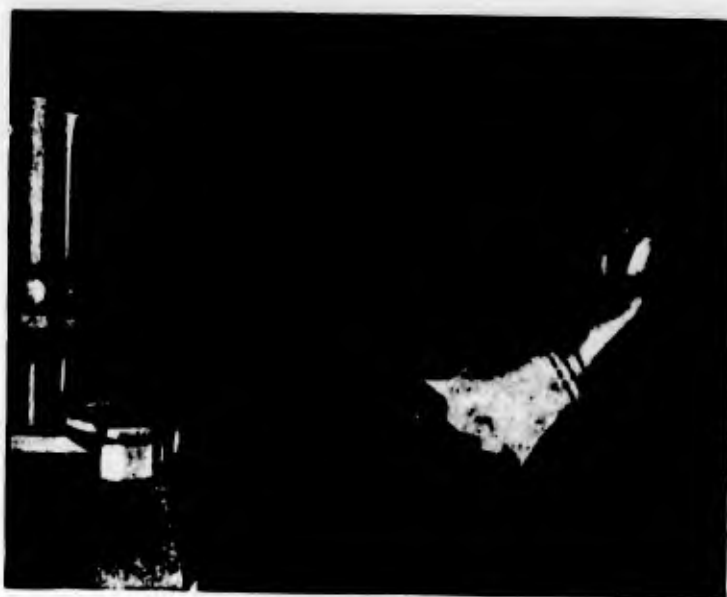
Fig. 145. Operation of jet induction meter with jet ignition.

TABLE 107

Ignition-Lag Relationships for Butylmercaptan — 98% HNO_3 Propellant

Temperature, °C	Chamber pressure, atm	Ignition lag, sec	Nature of process
+22	1	0.035	Combustion
−37	1	0.40	Explosion
+21	0.060	0.072	"
+22	0.065	0.095	"

ZhRD motors are employed to measure ignition lag; they have a thrust of about 25 kg [11]. The motor chamber is made from a transparent plastic, and has an inside diameter of 50 mm. There are two jet nozzles in the chamber head; they produce streams intersecting at a distance of 18 mm. The propellant components are supplied from thermostat-controlled tanks holding 100 and 200 ml under compressed-helium pressure. When pressure is applied to the propellant lines, membranes rupture, and the oxidizer and combustible pass through them to the combustion chamber where they ignite spontaneously upon contact.

In order to study the self-ignition process under high-altitude conditions, the nozzle section of the motor is connected to a chamber

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in which a rarefied atmosphere is set up corresponding to a flight altitude of 20-30 km. The processes of ignition and combustion are recorded with the aid of a high-speed camera at a rate of 6000 frames per second.

It is necessary to study the process of propellant self-ignition at low pressures in order to develop the high-power ZhRD installations used for aircraft.

For a propellant consisting of butylmercaptan and 9% nitric acid, the data shown in Table 107 were obtained for the ignition lag as a function of temperature and pressure.

Both at low temperature and low pressure, the starting of a liquid engine is hindered, although the difficulties arising may be overcome.

5. Composition of Hypergolic Propellants and Their Characteristics

As we have already stated, systems based upon organic compounds (amines, heterocyclic compounds, etc.) and nitric acid may be used as hypergolic propellants.

Table 108 gives the ignition lags for several combustibles with 98% nitric acid [12].
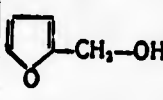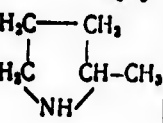
In order to determine the mean value with an induction meter, 7-8 parallel experiments are carried out. Experiments indicate that alkylation of aniline in an amino group increases the ignition lag. Furfuryl alcohol has the least ignition lag, and may be used as a base for hypergolic fuels in combination with amines.

The diene hydrocarbon dicyclopentadiene has the shortest ignition lag with nitric acid.

Using samples of basic self-igniting combustibles such as furfuryl alcohol and aniline, and also a sample of α-methylpyrrolidine, a study has been made of the effect of combustible-component relationships,

TABLE 108

Ignition Lags for Various Combustibles with Concentrated Nitric Acid [12]

1 Горючее	2 Формула	3 Задержка самовоспламенения, сек.								Среднее значение, сек.
		1 опыт 13	2 опыт 13	3 опыт 13	4 опыт 13	5 опыт 13	6 опыт 13	7 опыт 13	8 опыт 13	
4 Фурфуриловый спирт	(ring)$-CH_2-OH$	0,012	0,013	0,012	0,012	0,012	0,011	0,012		0,012
5 Анилин	$C_6H_5NH_2$	0,062	0,054	0,058	0,065	0,063	0,065	0,069		0,061
6 Метиланилин	$C_6H_5NHCH_3$	0,087	0,131	0,072	0,088	0,0110	0,078	0,163	0,153	0,115
7 Диэтиланилин	$C_6H_3N(C_2H_5)_2$	0,059	0,059	0,059	0,056	0,064	0,051	0,066	0,065	0,059
8 α-Метилпирроли-дин	(structure) H_2C-CH_2, H_2C $CH-CH_3$, NH	—	—	—	—	—	—	—	—	0,044
9 Дициклопента-диен	$C_{10}H_{12}$	—	—	—	—	—	—	—	—	0,032
10 Дициклопентадиен:										
11 с 5% меланжа	—	—	—	—	—	—	—	—	—	0,025
12 с 15% меланжа	—	—	—	—	—	—	—	—	—	0,011

1) Combustible; 2) formula; 3) ignition lag, sec; 4) furfuryl alcohol; 5) aniline; 6) methylaniline; 7) diethylaniline; 8) α-methylpyrrolidine; 9) dicyclopentadiene; 10) dicyclopentadiene; 11) with 5% melange; 12) with 15% melange.

temperature, and nitric-acid concentration upon the ignition lag. The physicochemical properties of the self-igniting components are given below:

1 Фурфуриловый спирт	Анилин 2	α-Метил- 3 пирролидин
4 Молекулярный вес	08,1	93,8	85,0
5 Плотность ...	1,133	1,022	0,804
6 Т. пл., °C ...	—30	—6,2	—
7 Т. кип., °C ...	170	180,4	81,8

1) Furfuryl alcohol; 2) aniline; 3) α-methylpyrrolidine; 4) molecular weight; 5) density; 6) melting point, °C; 7) boiling point, °C.

Figure 146 shows the change in the ignition lag with nitric acid as a function of mixture composition for: furfuryl-alcohol-aniline,

α-methylpyrrolidine-aniline, furfuryl alcohol-α-methylpyrrolidine, and also for mixtures containing all three components (Fig. 147).

The ignition lag does not vary additively with mixture composition, but is characterized by concave curves with a minimum for a specific composition. This minimum occurs for the following mixtures:

	Content, %	Ignition lag, sec
1. Furfuryl alcohol........	60-70	0.008
Aniline................	30-40	
2. Methylpyrrolidine.......	70-80	0.009
Aniline................	20-30	
3. Furfuryl alcohol........	30	0.012
Methylpyrrolidine........	70	

Three-component mixtures of combustibles do not have more favorable ignition lags than two-component mixtures. Curves for these systems are plotted from points found as averages from ten determinations.

The nitric-acid concentration has a substantial effect upon the ignition lag. Acid concentration has the greatest effect for the less active combustibles such as furfuryl alcohol as compared with the combustible consisting of 20% aniline and 80% furfuryl alcohol. Nitric acid concentration in the 96-99% range has no noticeable effect upon the induction period at normal temperature.

With a drop in the temperature of the propellant components, the ignition lag rises to various degrees depending upon the activity of the combustible. Figure 154 shows the variation in the ignition lag for a mixture of furfuryl alcohol (80%) with aniline (20%) and 93.5% nitric acid, depending upon temperature in the -30 to 30° range. For self-igniting combustibles to be used in ZhRD, the ignition lag with nitric acid should not exceed 0.03-0.04-0.05 sec at -30, -40° [9].

The increase in ignition lag with decreasing temperature is connected both with the lower rate of chemical reaction and with the in-

Fig. 147. Self-ignition lag as a function of composition in ternary furfuryl alcohol-methylpyrrolidine-aniline mixtures. Fa + Me) Combustible consisting of furfuryl alcohol and methylpyrrolidine; An) aniline; Fa) furfuryl alcohol; Me) methylpyrrolidine. 1) Fa; 2) An; 3) self-ignition lag, msec.

Fig. 146. Self-ignition lag of combustibles with concentrated HNO₃ as a function of composition. Fa) Furfuryl alcohol; An) aniline; Me) methylpyrrolidine. 1) Fa; 2) An; 3) self-ignition lag, msec.

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creasing viscosity of the mixture components, which impairs mixing.

The quality of component mixture has a large influence upon self-ignition. Thus, where the concentrated nitric acid is supplied to the combustible in the form of drops of various sizes, a decrease in acid drop size below 5 mm will lead to an increase in the ignition lag (especially at low temperatures).

In addition to the hypergolic furfuryl alcohol-aniline propellant, a hypergolic triethylamine-m-xylidine propellant has found employment. Technical xylidine is obtained from m-xylol, and contains 50-60% of the 2,4-dimethylaniline isomer:
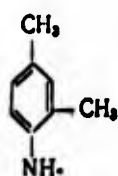
Figure 148 shows the influence of the triethylamine and xylidine proportions upon the ignition lag with 98.8% nitric acid. Minimum lag is observed where the mixture contains 60% triethylamine and 40% xylidine by volume.

These compounds have the following physical properties:

	1 Удельный вес	2 т. пл., °C	3 т. кип., °C	4 Теплота образования, ккал/моль
5 Триэтиламин . .	0,720	—114,8	89,5	+42,33
6 Ксилидин (2,4-диметиланилин) .	0,978	—	213	+46,2
7 Анилин	1,022	—6,2	154	—7,08
8 Фурфуриловый спирт	1,13	—32	171	+63,1

1) Specific gravity; 2) melting point, °C;
3) boiling point, °C; 4) heat of formation,
kcal/mole; 5) triethylamine; 6) xylidine
(2,4-dimethylaniline); 7) aniline; 8) fur-
furyl alcohol.

Optimum mixture composition will correspond roughly to the equilibrium relationship of the two substances.

A hypergolic propellant having a low ignition lag (0.02 sec) may be obtained from mixtures of triethylamine and aniline with 98.8% nitric acid (Fig. 149).

The effect of nitric acid composition upon the ignition lag of a combustible consisting of 60% by volume of triethylamine and 40% by volume of xylidine is shown in Fig. 150.

The ignition lag for the triethylamine-xylidine propellant called "Tonka-250" in the literature can be decreased by introducing catalysts into the nitric acid: salts of iron, copper, nickel, chromium, etc. [12].

Figure 151 shows the effect of the amount of catalyst added to 96.4% nitric acid upon the ignition lag of this fuel.

A mixture of dissolved salts having the composition Fe — 75%, Cr — 15%, Ni — 10% is added to the nitric acid as a catalyst.

For nitric acid containing up to 1% of the catalyst (in the form of a metal), the ignition lag drops from 0.021 to 0.013 sec.
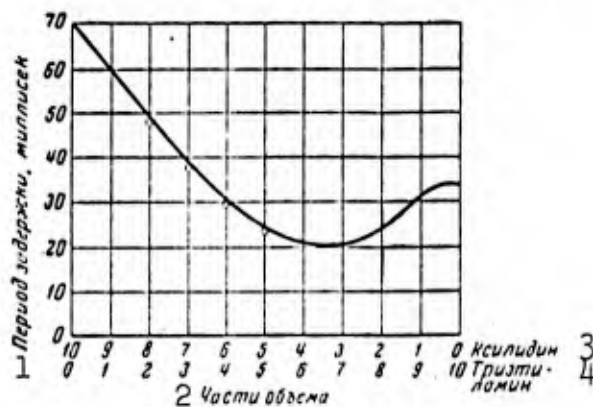
Fig. 148. Influence of composition of the self-igniting combustible triethylamine-xylidine on self-ignition lag with 98.8% nitric acid. 1) Lag, m/sec; 2) parts by volume; 3) xylidine; 4) triethylamine.
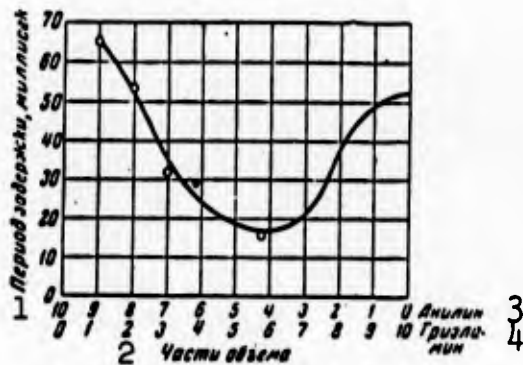
Fig. 149. Influence of composition of
self-igniting triethylamine-aniline com-
bustible on self-ignition delay with
98.8% nitric acid. 1) Lag, msec; 2) parts
by volume; 3) aniline; 4) triethylamine.
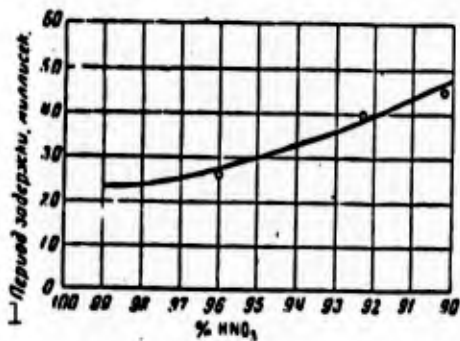
Fig. 150. Influence of nitric-
acid concentration on self-igni-
tion lag of combustible consist-
ing of 60% $(C_2H_5)_3N$ and 40%
$(CH_3)_2C_6H_3NH_2$. 1) Lag, msec.
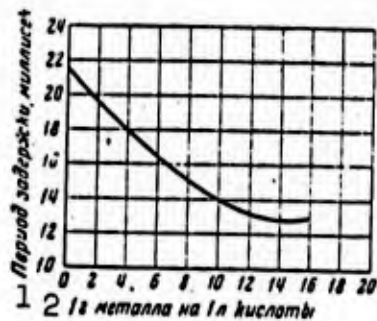
Fig. 151. Influence of amount of
catalyst on self-ignition lag of
propellant consisting of 96.4%
nitric acid and a 60-40 mixture
of triethylamine and xylidine. 1)
Lag, msec; 2) grams of metal per
liter of acid.
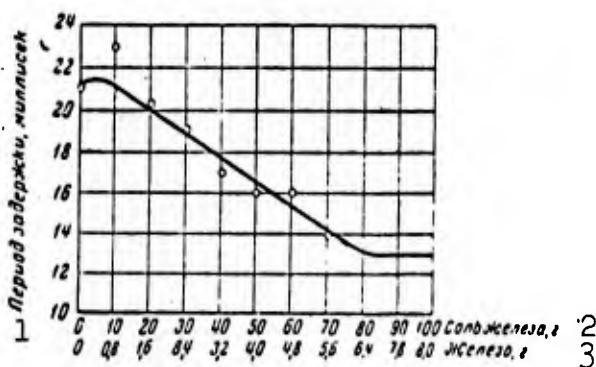
Fig. 152. Influence of amount of iron
dibutylnaphthalene sulfonate in solution
of combustible [$(C_2H_5)_3N - 60\%$,
$(CH_3)_2C_6H_3NH_2 - 40\%$] on self-ignition
lag with 98.8% nitric acid. 1) Lag, msec;
2) iron salt, g; 3) iron, g.

A similar effect may be achieved by adding iron salts of a sulfo
acid to a mixture of xylidine with triethylamine; the salts are dis-
solved in this combustible. Iron dibutylnaphthalene sulfonate
$[(C_4H_9)_2C_{10}H_5SO_3]_2Fe$ is used for this purpose.

To achieve the same effect, it is necessary to introduce up to 8 g
of Fe per liter of combustible (Fig. 152).

The use of nitric acid activated by catalysts (metals) evidently
makes it possible to create inexpensive self-igniting combustibles —
mixtures of amines with petroleum products.

Thus, the mixture consisting of 60% xylidine and 40% kerosene ig-
nites spontaneously with 95% nitric acid containing 1% iron, with an
ignition lag of 0.034 sec.

Table 109 shows the ignition lag for such mixtures.

TABLE 109

Ignition Lag for Mixtures of
Xylidine with Kerosene and 95%
Nitric Acid with 1% Iron

1 Состав горючего, %		Период задержки самовоспламенения, сек.
2 ксилидин	3 керосин	4
100	—	0,018
80	20	0,020
75	25	0,021
70	30	0,022
65	35	0,028
60	40	0,034
50*	50*	0,040
70	6 30% автобензина	0,047
5 (Триэтиламин ксилидин) —70	30	0,043

*The propellant does not ignite
without a catalyst.

1) Composition of combustible;
2) xylidine; 3) kerosene; 4)
ignition lag, sec; 5) (tri-
ethylamine xylidine); 6) motor
fuel.

Self-igniting combustibles may be obtained by adding 40-50% of

$C_nH_{2n+1}PH_2$ and $(C_nH_{2n+1})_3P$ type alkylphosphines to kerosenes. If products of pyrolysis are used as the hydrocarbon component, 25-30% alkylphosphine is sufficient. The mixture consisting of 30% hexylphosphine $C_6H_{13}PH_2$ and 70% pyrolysis products ignites spontaneously at -40° with a lag of 0.04 sec.

The results of interesting investigations dealing with a direct determination of the ignition lag for reaction fuels of various composition in chambers of liquid reaction engines have been published [13].

Table 110 shows the results of these investigations.

Such primary aromatic amines as aniline and xylidine when added to furfuryl alcohol reduce the ignition lag of the combustible with nitric acid. Tertiary amines in both the aromatic and aliphatic group increase the ignition lag.

During the Second World War, employees of the I.G. Farbenindustrie Company of Germany developed self-igniting combustibles consisting of cyclohexylamine and aniline [12]. As a result, recipes were proposed for combustibles which with 96-98% nitric acid, activated by iron, ignite spontaneously at -40°. The composition and properties of these combustibles are given below.

Content, %	"Hypergol-10"	"Hypergol-14"
cyclohexylamine..........	50.5	48.7
aniline.................	27.2	26.5
crude benzene...........	22.3	—
tetralin................	—	24.8
Pour point, $^\circ$C.............	−40	−40
Viscosity at -40°, centistokes..................	20	36.8
Heating yield, kcal/kg......	1427	—

Of the well-known self-igniting combustibles, the following recipes deserve the most attention: I. Furfuryl alcohol — 70%, aniline — 30% (Figs. 153 and 154). II. Triethylamine — 50%, xylidine — 50%.

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TABLE 110

Effect of Combustible Composition (Furfuryl Alcohol-Amines) upon Ignition Lag with 98% Nitric Acid in Chamber of ZhRD [13]

1 Горючее	2 Содержание, %	3 Формула	4 Период самовоспламенения, сек	5 Отношение окислителя-горючее
6 Фурфуриловый спирт	—	$-CH_2-OH$ (фуран)	0,033	1,21
7 Фурфуриловый спирт	75	$-CH_2-OH + C_6H_5NH_2$	0,018	1,31
8 Анилин	25			
9 Толуидин	25	NH_2, CH_3 + $-CH_2OH$	0,037	1,32
10 Фурфуриловый спирт	75			
11 Диметиланилин	25	CH_3-N-CH_3 + $-CH_2OH$	0,096	1,41
12 Фурфуриловый спирт	75			
13 Ксилидин	25	$CH_3, -NH_2, -CH_3$ + $-CH_2OH$	0,020	1,40
14 Фурфуриловый спирт	75			
15 Ксилидин	50	То же	0,027	1,5
16 Фурфуриловый спирт	50			
17 Диэтиланилин	25	$C_2H_5-N-C_2H_5$ + $-CH_2OH$	0,055	1,17
18 Фурфуриловый спирт	75			
19 Триэтиламин	25	$N(C_2H_5)_3$ + $-CH_2OH$	0,061	1,75
20 Фурфуриловый спирт	75			

1) Combustible; 2) content, %; 3) formula; 4) ignition lag, sec; 5) oxidizer-combustible ratio; 6) furfuryl alcohol; 7) furfuryl alcohol; 8) aniline; 9) toluidine; 10) furfuryl alcohol; 11) dimethylaniline; 12) furfuryl alcohol; 13) xylidine; 14) furfuryl alcohol; 15) xylidine; 16) furfuryl alcohol; 17) diethylaniline; 18) furfuryl alcohol; 19) triethylamine; 20) furfuryl alcohol.

The second combustible is known under the name "Tonka-250."

Together with concentrated nitric acid, combustibles I and II ignite with an ignition lag of less than 0.03 sec. They are characterized by acceptable physicochemical properties, and they may be produced on

an adequate scale from available raw materials.

It is known that the self-igniting furfuryl alcohol-aniline com-
bustible was initially utilized (1952) as the starting combustible in
the American interceptor rocket "Nike-1." It was placed in the main
combustible line, and provided instantaneous starting of an engine
that uses a nonself-igniting combustible [14].

In view of the fact that this combustible frequently became gummy
upon extended storage, it was replaced by an improved self-igniting
combustible — dimethylhydrazine (see below).

In order to expand the propellant raw-material base, in many cases
petroleum products or other hydrocarbon components are added to a self-
igniting synthetic combustible.

In this case, it is necessary to increase the activity of the ox-
idizer or combustible, which is done by adding activators or catalysts.
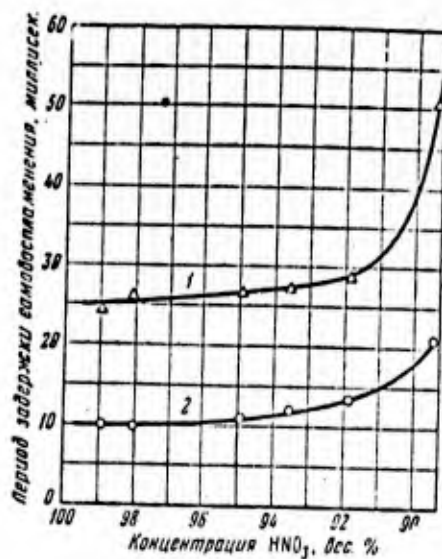
Fig. 153. Influence of nitric-
acid concentration on self-
ignition lag with various com-
bustibles. 1) Furfuryl alcohol;
2) 80% furfuryl alcohol and 20%
aniline. A) Self-ignition lag,
msec; B) HNO_3 concentration, %
by weight.

Thus, the addition of 10% sulfuric acid to 98% nitric acid increases its activity with respect to the self-ignition reaction. With such nitric acid, it is possible for turpentine, which basically consists of α-pinene, to ignite spontaneously. With standard nitric acid, turpentine will not ignite spontaneously.

The greatest activity is shown by an oxidizer consisting of nitric acid, sulfuric acid, and perchloric acid (14): $HNO_3 - 89\%$, $H_2SO_4 - 1\%$, $HClO_4 - 10\%$ (specific gravity 1.615).

Turpentine will ignite spontaneously with this oxidizer, even when mixed with kerosene, alcohols, or acetone. Aniline, xylidine, and furfuryl alcohol ignite spontaneously with a HNO_3-$HClO_4$ oxidizer, with a short lag.

	Ignition lag, sec	
	Nitric acid (98%)	Mixture of nitric acid (90%) + perchloric acid (10%)
Furfuryl alcohol......	0.021	0.005
Xylidine..............	0.062	0.03
Aniline...............	0.06	0.03

For a residual pressure of 250 mm Hg and a temperature of -38°, furfuryl alcohol ignites spontaneously with an oxidizer containing perchloric acid, with a lag of 0.013 sec.

It has been proposed that a mixture of pyrrole and ethyleneimine be used as a self-igniting combustible with nitric acid, having a very short lag at low temperatures.

The mixture of pyrrole and ethyleneimine has a low pour point and an ignition lag that is less than that for any of its components:

1 Пиррол, %	2 Этиленимин, %	3 Температура застывания, °C	4 Задержка самовоспламенения, сек.
90	10	—33	0,009 (при 24°)
80	20	—30	0,007 (при 24°)
80	20	—	0,011 (при—40°)
75	25	—62	0,008 (при—40°)

1) Pyrrole, %; 2) ethyleneimine; 3) pour
point, °C; 4) ignition lag, sec.

Recently [14] information has appeared on hypergolic propellants
based upon nitric acid, oxides of nitrogen, and combustibles contain-
ing hydrazine and methylhydrazine as the active initiators of self-
ignition. Thus, the ignition lag for a hydrazine-aniline propellant
with nitrogen tetroxide varies as a function of composition as follows:

1 Содержание, %		2 Период задержки само-воспламенения с N_2O_4, сек.
3 гидразин	4 анилин	
0	100	0,35
20	80	0,003
60	40	0,012
80	20	0,076

1) Content, %; 2) ignition lag
with N_2O_4, sec; 3) hydrazine;
4) aniline.
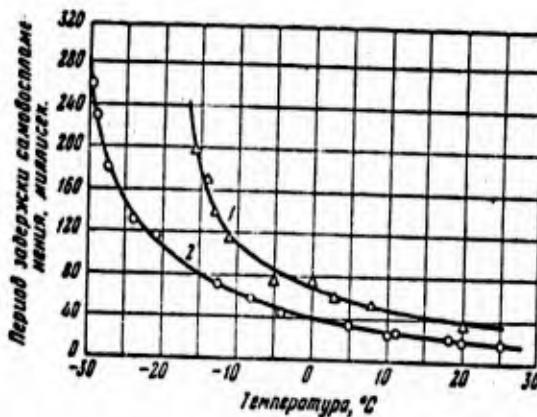
Fig. 154. Influence of temperature on
self-ignition lag of propellants. 1)
Nitric acid (93.5%) + furfuryl alcohol;
2) nitric acid (93.5%) + mixture of fur-
furyl alcohol (80%) with aniline (20%).
A) Self-ignition lag, msec; B) tempera-
ture, °C.

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As the data given shows, the addition of 20% hydrazine to aniline decreases the ignition lag by nearly a factor of ten.

Triethylamine, which enters into self-igniting combustibles, is obtained by amination of ethyl alcohol by ammonia under a pressure of 40-50 atm and at a pressure of 300-400° over a catalyst containing oxides of aluminum, tungsten, etc.

The reaction occurs with the formation of all three possible amines:

$$C_2H_5OH + NH_3 \rightarrow C_2H_5NH_2 + H_2O$$
$$2C_2H_5OH + NH_3 \rightarrow (C_2H_5)_2NH + 2H_2O$$
$$3C_2H_5OH + NH_3 \rightarrow (C_2H_5)_3N + 3H_2O.$$
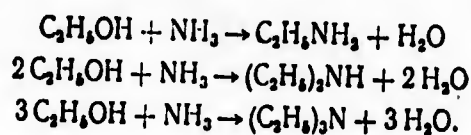
The mixture of amines contains from 5 to 20% triethylamine. After separation of water and the unreacted ammonia, the mixture of amines is disproportionated in order to convert the mono- and diethylamines to triethylamine. This reaction is carried out at 350° under a pressure of 20-50 atm over aluminum oxide, and is promoted by metals.

The following reactions occur here:

$$C_2H_5NH_2 + C_2H_5NH_2 \rightleftarrows (C_2H_5)_2NH + NH_3$$
$$(C_2H_5)_2NH + (C_2H_5)_2NH \rightleftarrows (C_2H_5)_3N + C_2H_5NH_2.$$
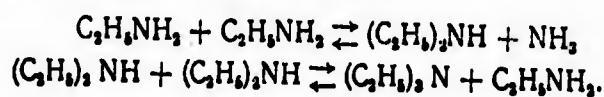
The amine mixture consisting of $(C_2H_5)_3N$ – 35-36%, $(C_2H_5)_2NH$ – 36-38%, $C_2H_5NH_2$ – 24-26%, is distilled.

Triethylamine boils at a temperature of 89.5°, diethylamine at 58°, and monoethylamine at 19°.

In Germany, an interesting method has been developed for synthesizing triethylamine by the combined hydration of acetonitrile and acetaldehyde. The basic reaction may be represented by the equation

$$CH_3 - C \equiv N + 2CH_3 - C{\overset{O}{\underset{H}{\diagup}}} + 4H_2 \xrightarrow[220°]{NI} (C_2H_5)_3N + 2H_2O.$$
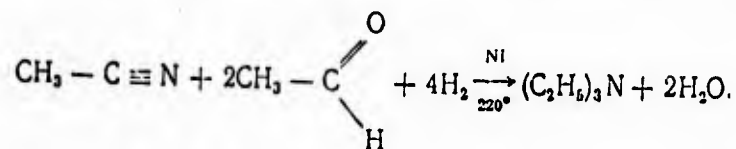
The amine mixture obtained from this reaction contains: triethyl-

amine — 62%, diethylamine — 24%, ethylamine — 14%.

Acetaldehyde is produced by direct synthesis from ethylene and oxygen:

$$C_2H_4 + \tfrac{1}{2}O_2 \xrightarrow{PdCl_2} CH_3 - C\!\!\begin{array}{c} {}^{\nearrow O} \\ {}_{\searrow H} \end{array}$$
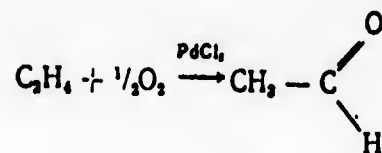
Acetonitrile may be obtained, with a good yield, from ammonia and pentane:

$$C_5H_{12} + NH_3 \xrightarrow[MoO_3]{600°} CH_3 - C \equiv N + 3C + 6H_2.$$
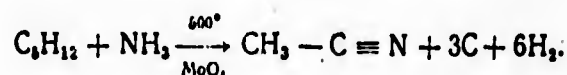
Triethylamine is also obtained from acetaldehyde and ammonia at $150°$ over a nickel-chromium-containing catalyst at atmospheric or slightly elevated pressure:

$$3CH_3 - C\!\!\begin{array}{c} {}^{\nearrow O} \\ {}_{\searrow H} \end{array} + NH_3 + 2H_2 \rightarrow (C_2H_5)_3N + 3H_2O.$$
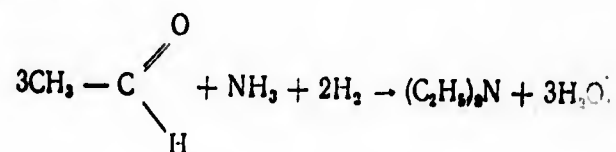
In practice, an amine mixture is formed which is disproportionated.

U.P. Vatsulek has described the direct synthesis of a mixture of ethylamines from ethylene and ammonia under the catalytic effect of metallic sodium or its hydride:

$$CH_2 = CH_2 + NH_3 \xrightarrow[820-980 \; atn]{200°} \begin{array}{l} CH_3 - CH_2 - NH_2 \\ (CH_3 - CH_2)_2NH \\ (CH_3 - CH_2)_3N \end{array}$$
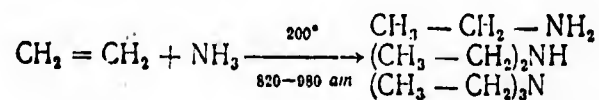
Diethylenetriamine which has recently been mentioned as a component of hypergolic propellants is obtained by reacting dichloroethane and ammonia under a pressure of 40-50 atm at $180°$:

$$ClC_2H_4Cl + NH_3 \begin{array}{c} {}^{\nearrow H_2N C_2H_4 NHC_2H_4 NH_2} \\ {}_{\searrow} \end{array}$$

triethylenepentamine, etc.
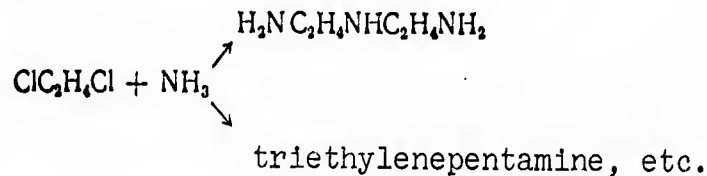
The yield of diethylenetriamine amounts to 40-50%.

Furfuryl alcohol which is contained in certain self-igniting com-

bustibles is obtained from furfurole, and the latter by hydrolysis of
pentosan:

$$(C_6H_8O_4)_x + xH_2O \xrightarrow{H_2SO_4} x\,C_6H_{10}O_6$$
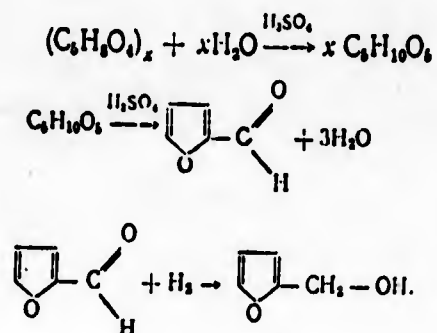
Pentosanes are contained in agricultural wastes: straw, sunflower
hulls, etc.

The intermediate product, furfurole, is used in the manufacture
of plastics.

Alkyl derivatives of hydrazine are used as active components of
hypergolic fuels: methylhydrazine, symmetric dimethylhydrazine, and
unsymmetric dimethylhydrazine, which is now receiving a great deal of
attention.

The physicochemical properties of the substances [15] are given
below:

1 Соединение	2 Формула	3 Плотность при 25°	4 т. пл., °C	5 т. кип., °C	6 Теплота образования, ккал/г-моль	7 Теплота горения, ккал/г-моль
8 Метилгидразин	CH_3NHNH_2	0,871	—52,4	87,5	—12,7	311,7
9 Симметричный диметилгидразин	$CH_3NHNHCH_3$	0,827	—8,9	81,5	—12,2	473,5
10 Несимметричный диметилгидразин	$\begin{array}{c}H_3C\\ \\ H_3C\end{array}\!\!\!>\!NNH_2$	0,783	—52	63,1	—11,3	472,6
11 Гидразин	H_2NNH_2	1,00	+2,0	113,5	—12,0	148,6

1) Content; 2) formula; 3) density at 25°; 4) melt-
ing point, °C; 5) boiling point, °C; 6) heat of
formation, kcal/g-mole; 7) heat of combustion,
kcal/g-mole; 8) methylhydrazine; 9) symmetric di-
methylhydrazine; 10) unsymmetric dimethylhydrazine;
11) hydrazine.

It has been proposed that phenylhydrazine $C_6H_5NHNH_2$ [16] be used
as a component of self-igniting combustibles for fuels based on nitric

acid, oxides of nitrogen, and tetranitromethane. A combustible consisting of a solution of anhydrous hydrazine in aniline has been suggested for this purpose.

It is evident that any interest presented by hydrazine and methylhydrazines will lie outside the framework of propellants based on nitric acid and hydrogen peroxide.

Propellants based on hydrazine, dimethylhydrazine, oxygen, and fluorine show very good energy characteristics.

In this connection, production of hydrazine and dimethylhydrazine has expanded in the United States during recent years.

Hydrazine is obtained from ammonia and hypochlorite:

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$
$$NH_2Cl + HNH_2 \rightarrow H_2N - NH_2 + HCl$$
$$NaOH + HCl \rightarrow NaCl + H_2O.$$
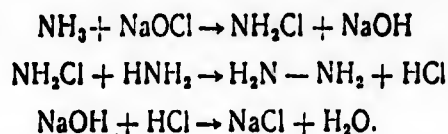
Various methods are used to obtain dimethylhydrazine on an industrial scale [17]. It may be obtained from dimethylamine and ammonia with the aid of sodium hypochlorite. In the first stage, the ammonia and sodium hypochlorite produce chloramine, while the chloramine and dimethylamine then produce dimethylhydrazine:

$$NH_3 + NaOCl \rightarrow NH_2Cl;$$
$$(CH_3)_2NH + ClNH_2 \rightarrow (CH_3)_2N - NH_2 + HCl.$$
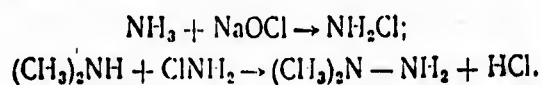
Dimethylamine may be obtained by alkylation of ammonia by methyl alcohol:

$$2 CH_3OH + NH_3 \rightarrow (CH_3)_2NH + 2 H_2O.$$
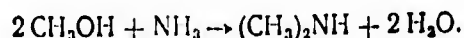
In another method, nitrosamine is obtained from the dimethylamine; the nitrosamine is then reduced further to dimethylhydrazine:

$$(CH_3)_2NH + NaNO_2 + HCl \rightarrow (CH_3)_2N - NO + NaCl + H_2O;$$
$$(CH_3)_2N - NO + 3H_2 \rightarrow (CH_3)_2N - NH_2 + H_2O.$$
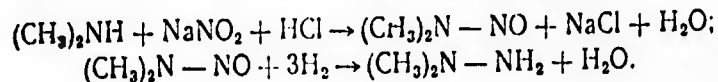
After removal of water and distillation of the reaction mass, 99% pure dimethylhydrazine is obtained.

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Dimethylhydrazine has a molecular weight of 60.08, a viscosity $\eta = 0.586$ centipoises, a heat capacity $C_p = 0.653$, a heat of formation of 187 kcal/kg, a heat of combustion of 7866 kcal/kg, a latent heat of vaporization of 193 cal/g, a critical temperature of 249°, and a critical pressure of 60 atm. The autoignition temperature of dimethylhydrazine with air is 250°. It mixes with water and gasoline in all proportions, and is toxic, although it is not a poison; great care should be exercised in working with dimethylhydrazine.

The technical specifications for dimethylhydrazine:

Content of unsymmetric dimethylhydra-
zine no less than.................. 98%
Specific gravity..................... 0.783-0.786
Melting point........................ -52°
Fractionation:
  10% distillation temperature..... 61.5^o
  90% distillation temperature..... 64.5^o

It is known that dimethylhydrazine is used together with oxygen in the second-stage motor for the United States "Vanguard" space rocket, which produces a thrust of 8 tons.

In the United States, dimethylhydrazine is used as a starting combustible for the "Nike" surface-to-air rockets; it is added to the kerosenes employed in the ZhRD with nitric acid in order to activate the combustion process.

The following self-igniting combustible mixtures based on dimethylhydrazine are recommended (in %):

$$
\begin{array}{lll}
\text{Aerozin} & \left\{ \begin{array}{l} H_2N - N(CH_3)_2 \ldots \ldots \\ H_2N - NH_2 \ldots \ldots \ldots \end{array} \right. & \begin{array}{l} 50 \\ 50 \end{array} \\
\text{Khaydin} & \left\{ \begin{array}{l} H_2N - N(CH_3)_2 \ldots \ldots \\ HN \begin{array}{l} C_2H_4NH_2 \\ C_2H_4NH_2 \end{array} \ldots \ldots \end{array} \right. & \begin{array}{l} 60 \\ 40 \end{array}
\end{array}
$$

This combustible, together with nitric acid containing 15% oxides of nitrogen, develops the following specific impulse (in sec) for a
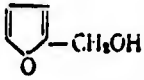
differential $p/p_0 = 50$:

RP-1 kerosene + nitric acid........ 247
Aerozine   "   " 257
Khaydin   "   " 253

TABLE 111

Ignition Lag of Propellants Based upon Hydrazine
and Nitric Acid in a Small Rocket Motor [13]

1 Горючее	2 Формула	3 Температура опыта, °C [4]	Окислитель	5 Период задержки самовоспламенения, сек.
7 Гидразин	N_2H_4	+21	[6] Конц. HNO₃ с 24% N_2O_4	0,0031 ± 0,0014
8 Гидразин	N_2H_4	+21	96%-ная NHO_3	0,005 ± 0,0017
9 Фурфуриловый спирт ..	⟨⟩—CH_2OH O	+21	[14] То же	0,0016 ± 0,0024
10 Гидразин	N_2H_4	—29 +25	, , 71,5%-ная HNO_3	От 0,022 до 0,040 0,037
11 Аммиак с добавкой 14% гидразина	$NH_3 + N_2H$	—36	[6] Конц. HNO₃ с 24% N_2O_4	0,006
12 Аммиак с 9,5% гидразина	$NH_3 + N_2H_4$	—35	То же 14	0,014
13 Аммиак с 5% гидразина	$NH_3 + N_2H_4$	от —37 до —47	, ,	0,037

1) Combustible; 2) formula; 3) experimental tem-
perature, °C; 4) oxidizer; 5) ignition lag, sec;
6) concentrated HNO_3 with 24% N_2O_4; 7) hydrazine;
8) hydrazine; 9) furfuryl alcohol; 10) hydrazine;
11) ammonia with addition of 14% hydrazine; 12)
ammonia with 9.5% hydrazine; 13) ammonia with 5%
hydrazine; 14) same.

For the "Titan" rocket, the propellant recommended consists of a mix-
ture of dimethylhydrazine and hydrazine: $(CH_3)_2N \cdot NH_2$ — 40-70%; N_2H_4 —
60-30% [17].

In 1954, dimethylhydrazine cost $13,000 per ton. With mass produc-
tion, it is assumed that its cost will not exceed $2200 per ton (the
cost of JP-4 petroleum aviation fuel is $7 per thousand liters).

Propellants containing hydrazine as a combustible have very short
ignition lags, measured in the thousandths of a second.

Table 111 shows the ignition lags in a rocket motor for various
propellants based upon hydrazine and nitric acid as a function of pro-
pellant composition and temperature.

TABLE 112

Effect of Adding 5% of Surface-Active
Substances upon Ignition Lag for
Self-Igniting Combustibles with 97%
Nitric Acid (Drop Method) [18]

1 Добавка	2 Период задержки самовос- пламенения, сек.	
	3 Фурфурило- вый спирт — 83%, нефтяное горючее—17%	Дициклопеп- тадиен—37%, нефтяное го- рючее — 63% 4
5 Нет	0,031	0,070
6 Амид олеиновой кислоты	0,023	0,039
7 Триэтаноламинолеат	0,023	0,031
8 Глицерилолеат	0,023	0,039
9 Цетилпиридинбромид	0,031	0,047
10 Натрийсульфорицинат	0,016	0,047
11 Натрийалкиларилсульфонат	0,023	0,047
12 Натрийалкилсульфат	0,023	0,031

1) Additive; 2) ignition lag, sec;
3) furfuryl alcohol — 83%, petroleum
combustible — 17%; 4) dicyclopenta-
diene — 37%, petroleum combustible —
63%; 5) none; 6) amide of oleic acid;
7) triethanolaminoleate; 8) glyceryl-
oleate; 9) cetyl pyridine bromide;
10) sodium sulforicinate; 11) sodium
alkyl aryl sulfonate; 12) sodium al-
kylsulfate.

TABLE 113

Effect of Adding 0.5% Surface-Active
Substances on Ignition Lag in a Mix-
ture of Furfuryl Alcohol (83%) and
Petroleum Combustible (17%) with
99.5% Nitric Acid (Jet Set-up) [18]

1 Добавка	2 Период задержки самовоспламене- ния, сек.
3 Нет	0,0263
4 Гликольолеат	0,0169
5 Цетилпиридинбромид	0,0200
6 Натрийнафталинсульфонат	0,0184
7 Натрийсульфорицинат	0,0195
8 Натрийалкилсульфат	0,0192

1) Additive; 2) ignition lag, sec;
3) none; 4) glycoleate; 5) cetyl pyr-
idine bromide; 6) sodium naphthylene
sulfonate; 7) sodium sulforicinate;
8) sodium alkyl sulfate.

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TABLE 114

Ignition Lag of Furfuryl Alcohol –
Nitric Acid Propellant with 0.5%
Surface-Active Substances as Addi-
tives [8]

1 Добавка	2 Период задержки, сек.	
	3 капельный метод	4 струйный метод
5 Нет	0,023	0,0299
6 Натриевая соль алкилсульфоната *, смешанная с горючим	0,023	0,0144
7 Натриевая соль алкилсульфата, смешанная с окислителем . . .	0,023	0,0227

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*Evidently of the ![C₁₁H₂₄ benzene ring with SO₃Na] type.
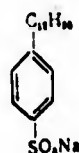
1) Additive; 2) lag, in sec; 3) drop
method; 4) jet method; 5) none; 6)
sodium salt of alkylsulfonate mixed
with combustible; 7) sodium salt of
alkyl sulfonate mixed with oxidizer.
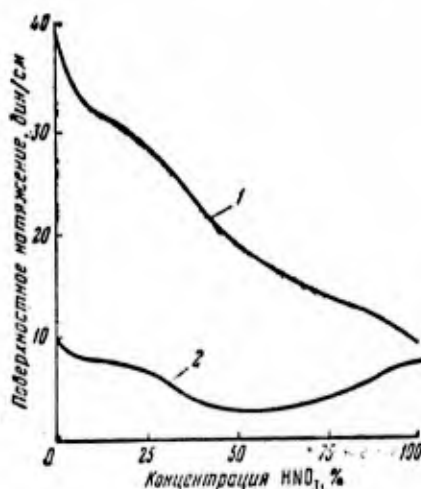
Fig. 155. Influence of surface-active
agent (sodium alkylaryl sulfonate) on
surface tension at phase boundary between
nitric acid and cyclohexane. 1) Nitric
acid-cyclohexane; 2) nitric acid-cyclo-
hexane + 1% sodium alkylaryl sulfonate.
A) Surface tension, dynes/cm; B) HNO_3

concentration, %.

In addition to the effect upon self-ignition of temperature, combustible composition, concentration of acid and catalysts, a study has recently been made of the role of physicochemical factors determining the rate of mixing of the components prior to the onset of the chemical reaction. These factors are the surface tension and viscosity of the propellant components.

The surface tension of combustibles may be changed by introducing small quantities of surface-active substances. The effect of surface-active substances upon the ignition lag of a combustible with 97% nitric acid is shown in Table 112.

The effect of surface active substances on the ignition lag in a jet installation is shown in Table 113.

Table 114 gives the ignition lags for furfuryl alcohol with 98% nitric acid determined by various methods under comparable conditions.

The surface tension at the nitric acid-cyclohexane phase interface in the presence of sodium salt of alkylsulfate [sic] appears in Fig. 155.

The results of the experiments depend upon both the method of determination and upon the method of adding the surface-active substance, which decreases the surface tension at the phase interface, and thus improves mixing of the reacting components and, consequently, their ignition as well.

6. Characteristics of Heating Value, Specific Thrust, and Combustion Temperature for Hypergolic Fuels

In addition to having good ignition and combustion properties, in operation, propellants should provide high exhaust velocity for the combustion products and high specific thrust, while the combustion temperatures should not be very high.

Tables 115 and 116 show the characteristics of these properties for propellants based upon nitric acid, nitric acid with oxides of nit-

TABLE 115

Characteristics of Nitric-Acid Based Propellants
[12, 19]

1 Топливо	2 Теплопроизводительность, ккал/кг	3 Удельный вес	4 Коэффициент избытка окислителя	5 Содержание горючего в топливе, %	6 Давление в камере, ат	7 Скорость истечения, м/сек	8 Удельный импульс, сек	9 Температура горения, °C
10 Азотная кислота + + жидкий водород	1885	0,61	—	—	21	2930	298	..
11 Азотная кислота с окислами азота + + анилин	—	1,37	0,93	24	21	2163	221	2796
12 Азотная кислота + + анилин	1440	—	0,9	26,6	21	—	218	2760
13 Азотная кислота + + фурфуриловый спирт	—	1,37	—	34,5	21	2120	214	2620
14 Меланж + моноэтиланилин	—	1,396	—	18,1	24	2060	210	2560
15 Азотная кислота + + гидразин	—	1,28	—	38,5	21	2390	243	—
16 Азотная кислота + + анилин	—	1,37	0,93	26,6	21	—	193	2759
17 Азотная кислота (60%), окислы азота (40%) + + анилин	1535	1,452	—	—	20	2205	225	2707

1) Propellant; 2) heating value, kcal/kg; 3) spe-
cific gravity; 4) excess-oxidizer factor; 5) com-
bustible content of propellant, %; 6) chamber pres-
sure, atm; 7) exhaust velocity, m/sec; 8) specific
impulse, sec; 9) combustion temperature, °C; 10)
nitric acid + liquid hydrogen; 11) nitric acid
with oxides of nitrogen + aniline; 12) nitric acid +
+ aniline; 13) nitric acid + furfuryl alcohol; 14) me-
lange + monoethylaniline; 15) nitric acid + hydra-
zine; 16) nitric acid + aniline; 17) nitric acid
(60%), nitrogen oxides (40%) + aniline.

rogen, and tetranitromethane.

In practice, the specific impulse of propellants based upon nit-
ric acid and amines at a chamber pressure of 21-25 atm is of the order
of 215-220 sec.

Figure 156 shows the effect of propellant composition upon the
specific impulse (specific thrust), combustion-product exhaust velocity,
and the combustion temperature.

Maximum specific impulse is obtained with a negative oxygen bal-
ance ($\alpha = 0.75$-0.85), where the combustion temperature is lower than
for the stoichiometric composition.

TABLE 116

Characteristics of Propellant Mixtures Based upon
Nitric Acid, Oxides of Nitrogen, and Tetranitro-
methane [19-21]

1 Топливо	2 Удельный вес	Теплопроизводительность, 3 ккал/кг	4 Температура горения, °C	5 Теоретическая скорость* истечения, м/сек	Теоретическая скорость* ракеты, м/сек 6
7 Керосин + азотная кислота	1,370	1375	2692	2140	1843
8 Керосин + азотная кислота (60%) и четырехокись азота (40%)	1,450	1472	2707	2180	1950
9 Анилин + азотная кислота	1,378	1440	2647	2175	1879
10 Анилин + азотная кислота (60%) и четырехокись азота (40%)	1,452	1535	2707	2205	1975
11 Анилин + тетранитрометан	1,502	1640	2922	2210	2025
12 Керосин + тетранитрометан	1,505	1590	2892	2190	2010
13 Водород + азотная кислота	0,605	1885	2612	2545	1257
14 Фурфуриловый спирт + азотная кислота	1,370	—	2770	2100	—

*For chamber pressure of 20 atm and nozzle section
pressure of 1 atm.

1) Propellant; 2) specific gravity; 3) heating
value, kcal/kg; 4) combustion temperature, °C; 5)
theoretical exhaust velocity, m/sec; 6) theoretical
rocket velocity, m/sec; 7) kerosene + nitric acid;
8) kerosene + nitric acid (60%) and nitrogen tet-
roxide (40%); 9) aniline + nitric acid; 10) ani-
line + nitric acid (60%) and nitrogen tetroxide
(40%); 11) aniline + tetranitromethane; 12) kero-
sene + tetranitromethane; 13) hydrogen + nitric
acid; 14) furfuryl alcohol + nitric acid.

The maximum specific impulse of a propellant consisting of nitric
acid and aniline corresponds to a ratio of oxidizer to combustible by
weight equal to three. At the same time, the stoichiometric composi-
tion of this propellant has a ratio close to four. Table 117 gives cal-
culated characteristics for propellants based upon nitric acid with
various contents of oxides of nitrogen and "T-250" combustible (50%
triethylamine and 50% xylidine), in accordance with the data of M.I.
Shevelyuk [22].

In order to increase the specific impulse in modern motors, there
is a pressure of 40-50 atm in the chamber, which yields an improvement
in the specific impulse of 20-25 units in comparison with the motors

TABLE 117

Specific Impulse of Propellant Based upon Triethylamine $(C_2H_5)_3N$ with Xylidine $(CH_3)_2C_6H_3NH_2$ and Nitric Acid with Oxides of Nitrogen [22]

1 Окислитель	2 Удельный импульс (сек.) при перепаде давления					
	20 am	30 am	40 am	50 am	60 am	60 am 3
4 Азотная кислота 98%-ная . . .	225	236	245	252	256	262
5 Азотной кислоты 80% . . . . . . } 6 Окислов азота 20% . . . . . . }	—	—	248	255	258	265
7 Азотной кислоты 60% . . . . . . } 8 Окислов азота 40% . . . . . . }	232	243	252	258	262	268

1) Oxidizer; 2) specific impulse (sec) for pressure drop of; 3) atm; 4) nitric acid (98%); 5) nitric acid (80%); 6) oxides of nitrogen (20%); 7) nitric acid (60%); 8) oxides of nitrogen (40%).
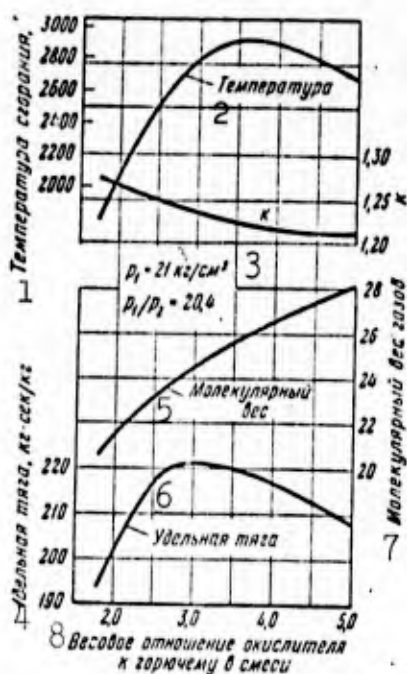
Fig. 156. Effect of proportions by weight of oxidizer and combustible (propellant of nitric oxide with 20% oxides of nitrogen + aniline) upon specific thrust and combustion temperature from design data (for chamber pressure of 21 atm). 1) Combustion temperature; 2) temperature; 3) kg/cm^2; 4) specific thrust, $kg \cdot sec/kg$; 5) molecular weight; 6) specific thrust; 7) molecular weight of gases; 8) ratio of weights of oxidizer and combustible in mixture.
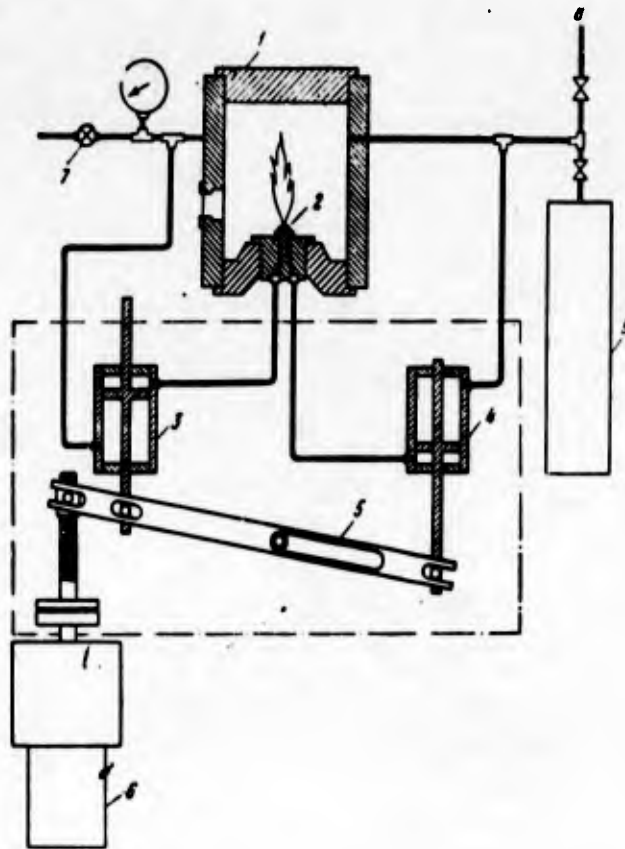
Fig. 157. Diagram of installation for studying combustion rate of hypergolic fuels. 1) Bomb with observation window; 2) two-component nozzle; 3) oxidizer supply (nitric acid); 4) combustible supply; 5) worm piston supply system for propellant component; 6) electric motor with worm transmission; 7) pressure reduction valve from nitrogen supply; 8) combustion-product exhaust; 9) sensor.

first designed.

7. Combustion Rate for Hypergolic Propellants

The combustion rate, together with the induction period, is the essential characteristic of a rocket propellant.

Recently, the literature has reported investigations of normal and turbulent combustion rates for a mixture of vapors of combustibles with air, oxygen, and oxides of nitrogen. Data on the combustion rates of hypergolic fuels is lacking.

In 1955, [23] was published; it presented a study of the combustion rate of hypergolic propellants under pressure for which a special, original installation was developed. This installation consisted of a
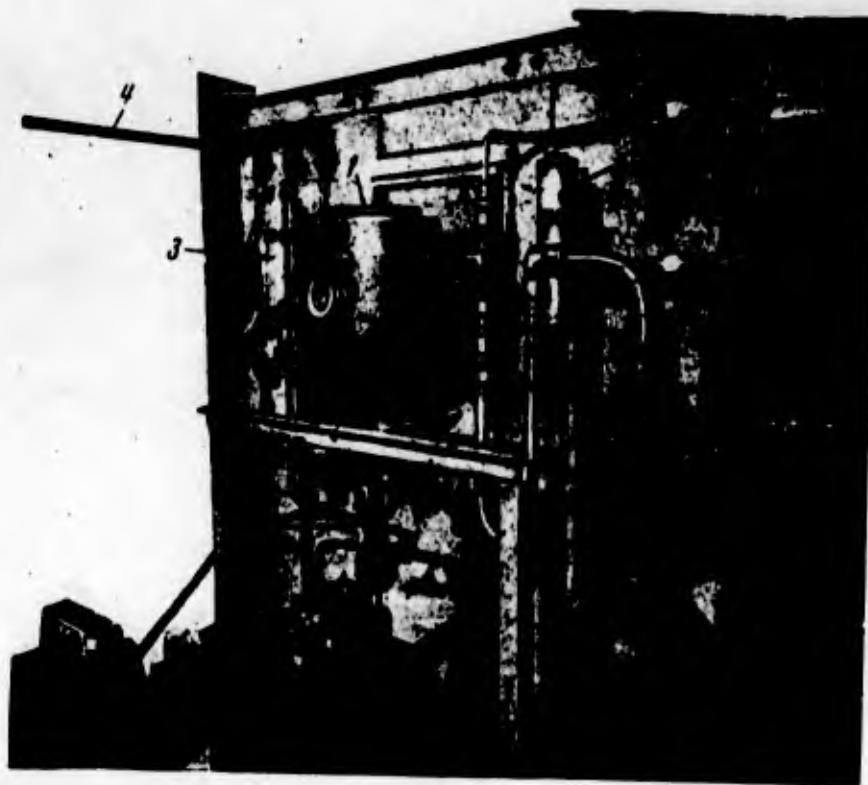
Fig. 158. Outside view of installation for studying combustion rate of hypergolic propellants. 1) Bomb for combustion; 2) tank with combustible; 3) tank with oxidizer; 4) nitrogen line; 5) pump.
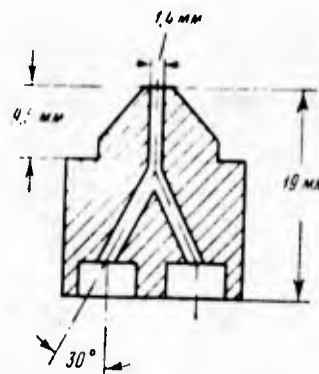
Fig. 159. Arrangement of two-component nozzle for studying the combustion rate of hypergolic propellants.

bomb containing a special burner. In the wall, there is an inspection window, covered with thick glass (Fig. 157). Oxidizer and combustible are supplied to the burner with the aid of a special supply system driven by a motor. The outside appearance of the installation is shown
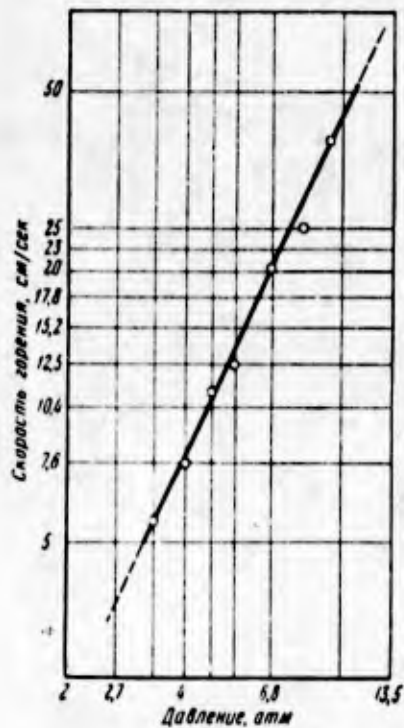
Fig. 160. Combustion rate for
hypergolic propellant mixture
of butylmercaptan-nitric acid
as a function of pressure. 1)
Combustion rate, cm/sec; 2)
pressure, atm.

Fig. 161. Nature of flame for
mercaptan-nitric acid propel-
lant upon combustion in bomb.

in Fig. 158. The arrangement of the two-component nozzle is shown in
Fig. 159.

The propellant components were a self-igniting combustible consisting of a mixture of mercaptans: propylmercaptan 27.8%, butylmercaptan 65.3%, amylmercaptan 6.6%, hexylmercaptan 0.3%.

This mixture was obtained from a petroleum refinery. 95.6% nitric acid was used as the oxidizer.

Using the 0.5 mm cross-section N76 nozzle, the combustion rate (flow rate) of the propellant will vary with pressure as shown in Fig. 160. In the 3.5 to 13.5 atm range, the combustion rate varies from about 5.0 to 70 cm/sec.

The combustion rate of hypergolic propellants is far greater than that of diergolic propellants. Figure 161 shows the nature of the flame given by this fuel.

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23. M. Cullough, H. Jenkins. 5th Symposium on Combustion. New York-London, 1955, p. 181; M.I. Shevelyuk. Teoreticheskiye osnovy proyektirovaniya zhidkostnykh reaktivnykh dvigateley [Theoretical Foundations for the Design of Liquid Reaction-Thrust Engines].
Moscow, Oborongiz, 1960.

Manu-script Page No.	[Footnote]
415	The salt-formation reaction yields 19 kcal, the dinitration 23 kcal, totaling 42 kcal.

Chapter 5

NONHYPERGOLIC HYDROCARBON NITRIC-ACID-BASED FUELS

Petroleum products generally do not ignite on their own at standard temperatures with nitric acid. Therefore, a special ignition system is required for engine starts, and the burning process is generally less stable than in the case of hypergolic combustibles. However, petroleum products offer a substantially greater base for the derivation of jet fuels than does any other form of raw material. Cracking-kerosenes and aviation kerosenes can be used as combustibles, as can other products from the processing of petroleum, coal, and shales.

In 1950-1952 reports began appearing in the press on the utilization of kerosene with nitric acid as a combustible (fuel) for rocket engines of experimental models designed to develop low thrust of up to 459 kg. Note was taken here of the substantially greater engine pulsation which occurred with the use of kerosene in comparison with hypergolic combustibles (fuels) [1, 2].

In 1955 it was announced that a fuel consisting of nitric acid and kerosene [3, 4] was being used in the engine, developing a thrust of 8-12 tons, of the American anti-aircraft radio-guided "Nike" rocket.

Thus kerosene with nitric acid has found application as a combustible (fuel) in rocket engines.

During the first stages of the development of rocket engineering, synthetic hypergolic combustibles with nitric acid were used in ZhRD (liquid rocket engines), since this made it easier to use the engines.

In connection with the interest expressed in petroleum products

as possible combustibles in fuels for rocket engines, investigations have been carried out on the interaction of hydrocarbons with nitric acid at various temperatures.

These works, published between 1952 and 1954, are of interest only from a theoretical standpoint and cannot be used directly for the establishment of engine cycles. However, they expand our range of knowledge about the reaction capacities of various hydrocarbons with respect to nitric acid, and this can be used to advantage in the selection of propellants (fuels).

1. Thermal Effect of the Interaction between Hydrocarbons and Nitric Acid

Among the hydrocarbons, only the diene and certain acetylene hydrocarbons ignite spontaneously on contact with nitric acid. For example, dicyclopentadiene is hypergolic with 99% nitric acid, exhibiting a lag of 0.032 seconds [5]. However, olefins, and aromatic and saturated hydrocarbons only heat up when mixed with nitric acid at standard temperatures, but do not ignite by themselves. In this connection, it has been proposed to characterize the reaction capacity of hydrocarbons in terms of the heating temperature of the hydrocarbon mixture with nitric acid.

In 1952, Trent and Zucrow published the results of their investigation [6] on the interaction of hydrocarbons with nitric acid at low and high temperatures. It was the purpose of their work, as the authors themselves point out, to study the behavior of certain pure hydrocarbons under conditions close to the conditions prevailing in a jet engine.

In mixing nitric acid exhibiting a concentration in excess of 90% with unsaturated hydrocarbons, a vigorous exothermic reaction similar to an explosion takes place, and this is particularly true in the case of polyolefins and acetylenic hydrocarbons. In this case, the tempera-

- 459 -
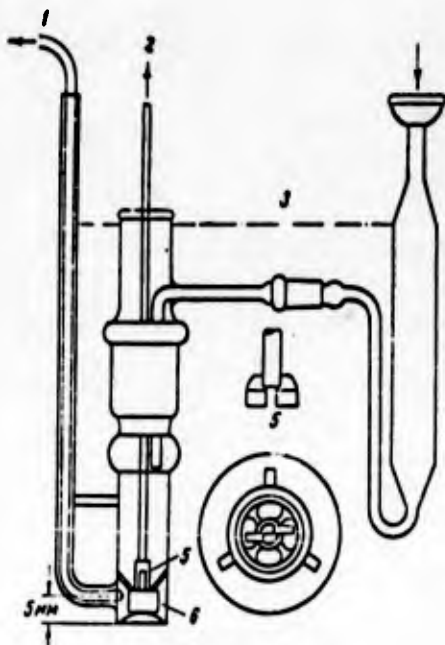
Fig. 162. Device for determina-
tion of temperature effect of
interaction between hydrocar-
bons and nitric acid. 1) Line
to oscillograph; 2) mixer
drive, with motor turning at
6000 rpm; 3) water level in
thermostat; 4) vessel for sup-
ply of HNO_3 under a nitrogen
pressure of 150 mm Hg; 5) agi-
tator; 6) cylinder guide to
agitator.

ture of the reaction attains its maximum within a short period of time.

Trent and Zucrow assume that the rate of heat liberation in the
reaction between the hydrocarbons and the nitric acid is proportional
to the rate of the reaction and may serve as a criterion for the com-
parison of relative liquid-phase reactions between hydrocarbons and
nitric acid.

Consequently, the maximum temperature attained during the interval
of time τ can give some indication of the reaction capacity of hydro-
carbons with nitric acid.

The temperature effect of the reaction produced by the interaction
of hydrocarbons with nitric acid was studied by these authors in the
device shown in Fig. 162.

The reactor is a tube made of borosilicate glass inside of which there is an agitator rotating at 6000 rpm. The agitator provides for the energetic mixing of the oxidizer with the combustible. The supply of nitric acid is carried out under a low pressure (155 mm Hg) from a vessel; the combustible is contained directly in the reactor; the temperature is measured by means of a platinum-platinorhodium thermocouple; the readings are recorded by means of an oscillograph. The total quantity of fuel components amounts to 5.4 ml, with an acid-to-hydrocarbon ratio of 3:1.

The results are presented in Table 119.

It follows from the data in Table 118 that the paraffinic hydrocarbons of normal structure (decane) do not react with nitric acid; monoolefins and cycloolefins react vigorously; diolefins with conjugate double bonds react most vigorously.

Aromatic hydrocarbons react less vigorously with HNO_3 than do the monoolefins, but more actively than do the naphthenes and paraffins. The above can be presented by the following series:

diolefins > olefins > aromatic hydrocarbons > > naphthenes > paraffins

The naphthenes interact with nitric acid with approximately the same heating as do aromatic hydrocarbons. However, the time required to attain the maximum temperature in the case of the naphthenes is longer by a factor of approximately 15-20 than is the case with the aromatic hydrocarbons.

Among the aromatic hydrocarbons, indene yields the greatest heating — 421° — and ignites within 1 to 2 seconds. This can be explained by the fact that one of the bonds in the five-member ring of indene is unsaturated.

Table 119 shows the temperature effect produced by the interaction

TABLE 118

Temperature Effect Produced by the Interaction of
Hydrocarbons with 100.2% Nitric Acid [6]
Initial Temperature, 25°

1 Углеводород	Максимальная температура, °C 2	Увеличение температуры Δt, °C 3	Время достижения максимальной температуры τ, сек 4
5 Алифатические углеводороды			
6 Децен-1	127,5	102,5	0,160
7 Декадиен-1,3	170,0	145,0	0,305
8 3-Метилнонен-3	128,5	103,5	0,320
9 Декадиен-1,3	166,0	141,0	0,535
10 Алициклические углеводороды			
11 Дициклопентадиен	25 Самовоспламенение		0,04
12 Циклогексен	110	85	0,24
13 Метилциклогексан	71	46	2,48
14 Этилциклогексан	80	55	2,55
15 Циклогексан	53	28	17
16 Ароматические углеводороды			
17 Бензол	92,5	67,5	0,100
18 Толуол	95,5	70,5	0,120
19 α-Метилнафталин	110	85	0,120
20 о-Ксилол	101	76	0,133
21 Мезитилен	122	97	0,163
22 Этилбензол	125	101	0,273
23 Изопропилбензол	124,5	99,5	0,352
24 Инден	44	396	3,170

1) Hydrocarbon; 2) maximum temperature, °C; 3) increase in temperature Δt, °C; 4) time required for attainment of maximum temperature, τ, in sec; 5) aliphatic hydrocarbons; 6) decene-1; 7) decadiene-1,3; 8) 3-m thylnonene-3; 9) decadiene-1,3; 10) alicyclical hydrocarbons; 11) dicyclopentadiene; 12) cyclohexene; 13) methylcyclohexane; 14) ethylcyclohexane; 15) cyclohexane; 16) aromatic hydrocarbons; 17) benzene; 18) toluene; 19) α-methylnaphthalene; 20) o-xylene; 21) mesitylene; 22) ethylbenzene; 23) isopropylbenzene; 24) indene; 25) self-ignition.

of nitric acid of reduced concentration (93.27%) with unsaturated hydrocarbons.

Acetylenic hydrocarbons react with nitric acid at approximately the same rate as do diolefins. The rate of cycloolefin interaction with nitric acid is greater than for olefins with an open chain, and this can be seen from the example of decene and the pinenes.

With a nitric-acid concentration below 95%, the rate of interac-

tion with decene-1 drops significantly.

Nitrogen dioxide, dissolved in 98% nitric acid, increases its rate of reaction with olefins. Thus, for example, the reaction between decene-1 and 95.86% nitric acid, containing 3.3% N_2O_4, attains its maximum temperature within 0.4 sec. However, this reaction with nitric acid (of the same concentration), but containing nitrogen oxides, requires 0.38 sec to attain the same evolution of heat.

Probably one of the initiating reactions is the combination of nitric acid to the double bond in the form $H-ONO_2$ with the formation of nitroethers. The presence of several peaks on the time-temperature curve indicates that the reaction involved several successive stages, each stage exhibiting its own rate and energy of activation.

TABLE 119

Temperature Effect Produced by the
Interaction of 93.27% Nitric Acid
with Unsaturated Hydrocarbons* [6]

	1 Углеводород	Максимальная температура, 2 °C	Увеличение температуры 3 Δt, °C	4 Время достижения максимальной температуры τ, сек.
5	Децен-1	109	82	0,166
6	Декадиен-1,3	116	86	0,170
7	Декадиен-1,9	124	94	0,197
8	Декадиен-1,9	120	92	0,475
9	Децен-1	105	80	0,770
10	α-Пинен	113	83	0,085
11	β-Пинен	122	92	0,152
12	Дициклопентадиен . . .	128	98	0,107

*The oxidizer-to-hydrocarbon ratio is 10.7; the nitric acid has the following composition: HNO_3, 93.2%; NO_2, 0.63%; H_2O, 6.11%.

1) Hydrocarbon; 2) maximum temperature, °C; 3) increase in temperature, Δt, °C; 4) time required to attain maximum temperature, τ, sec; 5) decene-1; 6) decadiene-1,3; 7) decadiene-1,9; 8) decadiene-1,9; 9) decene-1; 10) α-pinene; 11) β-pinene; 12) dicyclopentadiene.

2. Minimum Self-Ignition Temperature and Lag for Hydrocarbons with Nitric Acid

The self-ignition temperature and the self-ignition lag in the case of low ($\pm 40^{\circ}$) and high ($300-500^{\circ}$) temperatures are a measure of the reaction capacity of organic combustibles with respect to nitric acid.

TABLE 120

Thermal Self-Ignition Temperature and Lag for Combustibles with 98% Nitric Acid at High Temperatures [7]

1 Горючее	2 Низшая температура самовоспламенения, °C	3 Период задержки самовоспламенения (сек.) при температуре, °C		
		550	500	400
4 Триэтиламин	300	0,017	0,040	0,075
5 Фурфуриловый спирт	325	0,040	0,050	0,080
6 Фурфуриловый спирт (60%) + анилин (40%)	—	0,035	0,050	0,080
7 α-Пинен	350	0,025	0,045	0,093
8 Легкое масло пиролиза	430	0,050	0,060	0,093
9 Крекинг-керосин	425	0,050	0,065	0,120
10 Керосин прямой гонки Т-1	506	0,080	0,120	—

1) Combustible; 2) lower self-ignition temperature, $^{\circ}$C; 3) self-ignition lag (sec) at a temperature of, $^{\circ}$C; 4) triethylamine; 5) furfuryl alcohol; 6) furfuryl alcohol (60%) + aniline (40%); 7) α-pinene; 8) light oil of pyrolysis; 9) cracking kerosene; 10) kerosene produced by the direct distillation of T-1.

Under standard temperature conditions, petroleum products are not hypergolic with nitric acid, whereas the amines and dienic compounds ignite easily by themselves. However, at high temperatures ($300-400^{\circ}$) all combustible substances are hypergolic with nitric acid, with some lag. At $200-400^{\circ}$ this process begins with the vaporization of the substances, but in this state the hypergolic organic substances (for examples, the amines) ignite with nitric acid above $200-30^{\circ}$ [sic], and the petroleum products ignite at a higher temperature. The self-ignition temperature and lag, determined at high temperatures in nitric-

acid vapors, are referred to as the temperature and lag of "thermal hypergolic ignition." With certain limits, these are characteristics of fuel combustion in ZhRD (liquid rocket engines).
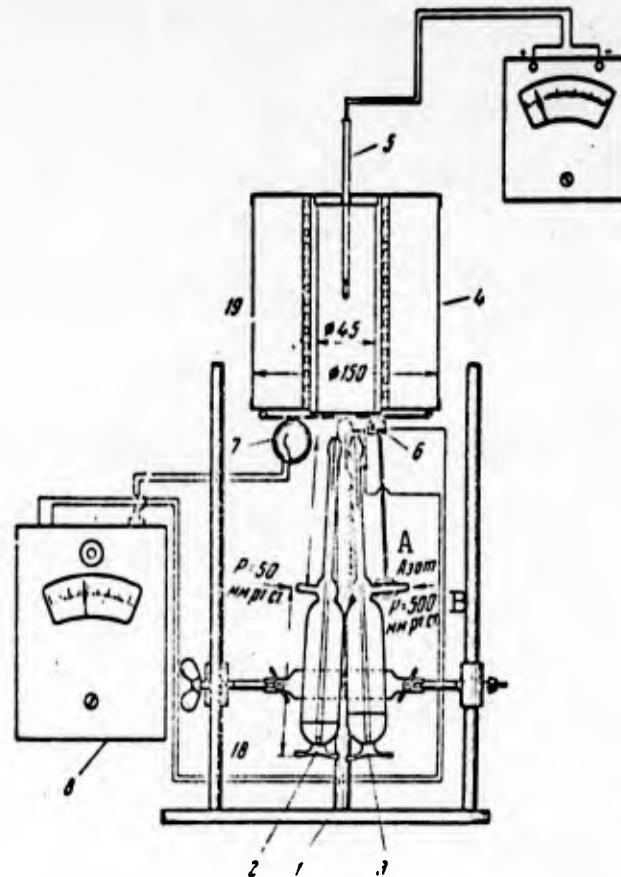
Fig. 163. Installation for the determination of thermal hypergolic ignition temperature and lag for liquid-reaction-engine propellants (fuels). 1) Support for mounting of instrument; 2 and 3) spray nozzles (injectors) for combustible and oxidizer; 4) electrically heated furnace; 5) thermocouple and galvanometer; 6) electrical sensor to establish instant of fuel feed (closed by nitric-acid stream); 7) photocell recording flash; 8) instrument recording hypergolic-ignition lag. A) Nitrogen; B) p = 500 mm Hg.

This method of ZhRD propellant characteristics was first proposed in 1951 by Ya.M. Paushkin [7], and subsequently in 1952 and 1954 there were brief reports by American investigators.

In the determination of the thermal period of induction according to the method of Ya.M. Paushkin [7], the components of the propellant,

in vaporized state, were fed into the heated furnace chamber by means of compressed nitrogen and here the hypergolic-ignition temperature and lag were determined. The installation for the determination of the thermal hypergolic-ignition lag is shown in Fig. 163.

The results obtained here are presented in Table 120.

The nature of the change in the periods of hypergolic-ignition lag for vapors of various combustibles in nitric-acid vapors as a function of temperature is presented in Fig. 164 [7]. For combustibles of greater reaction capacity (Tonka-250 — a mixture of 50% triethylamine with 50% xylidine), the curves in temperature-time coordinates are lower than the curves for combustibles of lower reaction capacities (direct-distillation kerosene, aromatic hydrocarbons).
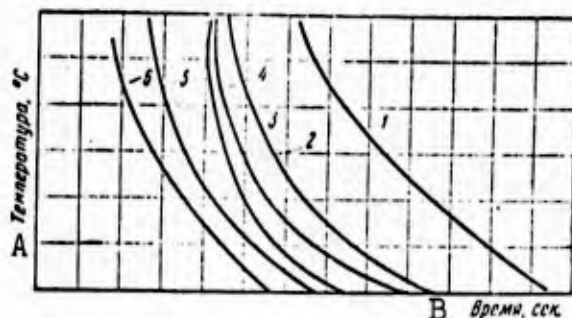
Fig. 164. Nature of change in thermal self-ignition lag for various combustibles in vapors of 98% nitric acid. 1) Aromatic hydrocarbons; 2) lamp kerosene; 3) n. paraffin; 4) T-1 kerosene; 5) cracking kerosene; 6) Tonka-250. A) Temperature, °C; B) time, sec.

The hypergolic ignition temperature and lag are not physical constants, since they are functions of the conditions under which the experiment is being carried out; but if they are determined under standard conditions they characterize the comparative activity of the fuels (propellants) and, apparently, reflect in qualitative terms the induction period in the ZhRD chamber: the higher the hypergolic ignition temperature and lag, the greater the propellant induction period in

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TABLE 121

Minimum Hypergolic Ignition Temperature for Combustibles Based on Hydrocarbons and Their Mixtures in Nitric Acid [6]
(HNO_3, 99.1%; N_2O_4, 0.39%; H_2O, 0.51%)

1 Горючее	2 Минимальная температура самовоспламенения, °C
3 Дициклопентадиен	12 Самопоспламеняется при отрицательной и обычной температурах
4 Дициклопентадиен (45%) + декан (55%)	8
5 » (35%) + » (65%)	85
» (30%) + децен-1 (70%)	143
» (25%) + декан (75%)	154
» (20%) + децен-1 (80%)	183
» (10%) + » (90%)	213
6 Децен (65%) + ксилол (15%) + метилнафталин (20%)	217
7 Мезитилен	398
8 Децен-1	302
9 п-Цимол	383
10 н. Декан	340
11 Авиационный керосин	370
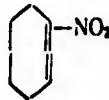
1) Combustible (fuel); 2) minimum hypergolic ignition temperature, °C; 3) dicyclopentadiene; 4) dicyclopentadiene (45%) + decane (55%); 5) dicyclopentadiene (30%) + decene-1 (70%); 6) decene (65%) + xylene (15%) + + methylnaphthalene (20%); 7) mesitylene; 8) decene-1; 9) p-isopropyltoluene; 10) n. decane; 11) aviation kerosene; 12) self-ignition occurs both in the case of negative and standard temperatures.

the ZhRD chamber.

The device used by Trent and Zucrow for the determination of the minimum hypergolic ignition temperature consisted of an aluminum block 75 mm in diameter and 200 mm long. A 500-watt heater, capable of maintaining a constant temperature by means of an electronic temperature regulator, was employed to heat the block. The propellant (fuel) components were fed to the heated block through two glass spray nozzles

TABLE 122

Products of the Reaction Between Olefins with Nitric Acid and Nitrogen Oxides [8]

1 Углеводород	2 Реагент	3 Условия	4 Продукт реакции
$CH_2=C-CH_2-CH_2-CH_3$ $\quad\;\; C_2H_5$	5 Азотная кислота (80%-ная)	70—75°	$CH_3-CH_2-CH_2-CH=C-CH_2-NO_2$ $\qquad\qquad\qquad\qquad C_2H_5$
$CH_2=CH-(CH_2)_4-CH_3$	6 То же	90—100°	$CH_2=C-(CH_2)_4-CH_3$ $\qquad NO_2$
$CH_2=CH_2$	Азотная кислота (95—100%-ная)	—	$HO-CH_2-CH_2-NO_2$
C_6H_{10}	Азотная кислота (96%-ная)	80°	$C_6H_{10}(NO_2)_2$
[cyclohexene ring]	7 Окислы азота	60—65°	[ring]$-NO_2$
$CH_2=CH-CH=CH_2$	То же	30°	$C_4H_6NO_2$
$CH_3-C=C-CH_3$ $\quad\;\; CH_3\;\; CH_3$	» »	8 В эфире	$CH_3-C——C-CH_3$ $\quad\; CH_3\; CH_3$ $\quad\;\; NO_2\;\; NO_2$
$CH_3-C=CH_2$ $\quad CH_3$	» »	То же	$CH_3-C——CH$ $\quad\; CH_3\;\; CH_3$ $\quad\;\; ONO_2\; NO_2$
$CH_3-C=CH_2$ $\quad CH_3$	» »	9 Без растворителя	CH_3-C-CH_2 $\quad\; CH_3$ $\quad\; NO_2-O\;\; NO$
$CH_2=CH-CH=CH_2$	» »	10 Растворители или паровая фаза	$CH_2-CH=CH-CH_2$ $\; NO_2\qquad\qquad NO_2$

1) Hydrocarbon; 2) reagent; 3) conditions; 4) reaction product; 5) nitric acid (80%); 6) the same; 7) nitrogen oxides; 8) in ether; 9) without solvent; 10) solvents or vapor phase.

(injectors) by means of compressed air. The streams of the two liquids impinged against one another not too far away from the heated block.

Table 121 shows the minimum hypergolic ignition temperature for hydrocarbon mixtures with nitric acid. This temperature was defined as the lowest furnace temperature at which fuel self-ignition occurred as the propellant came into contact with the heated surface. This temperature also serves as the criterion for a preliminary evaluation of hy-

drocarbon propellants for liquid reaction engines.

In certain cases, a parallelism is observed between the minimum hypergolic ignition temperature and the maximum quantity of heat evolved. However, this parallelism is not preserved throughout. In a number of cases, the hydrocarbon mixtures which exhibit the greatest temperature rise have minimum hypergolic ignition temperatures; in other cases, this quantitative relationship is not preserved.
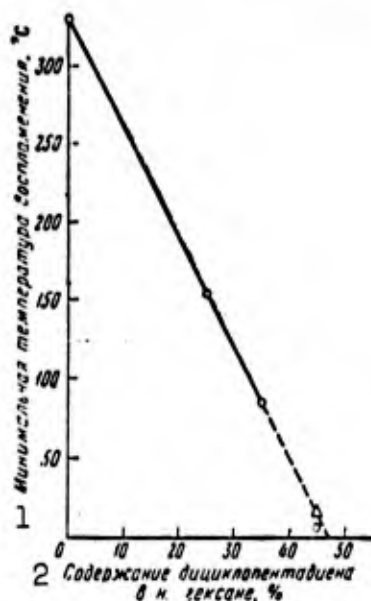
Fig. 165. Effect of additions of dicyclopentadiene on the hypergolic ignition temperature of a hexane-dicyclopentadiene mixture with concentrated nitric acid. 1) Minimum ignition temperature, $^{\circ}C$; 2) content of dicyclopentadiene in n. hexane, %.

Probably, the divergence in this case is associated with the mutual effect of thermal instability and the concentration of unstable chemical compounds formed during the reaction process.

The ease of ignition for unsaturated compounds can be explained by the fact that they react easily with the oxides of nitrogen and with nitric acid.

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The interaction of nitric acid and the oxides of nitrogen with olefins at low temperatures was studied during the nitration of these compounds (Table 122).

In the interaction of nitrogen oxides with olefins, depending on the conditions, four types of compounds are formed [8]:

$$
\begin{array}{llll}
-CH-NO & -CH-NO_2 & -CH-NO_2 & -CH-ONO \\
| & | & | & | \\
-CH-ONO_2 & -CH-ONO & -CH-NO_2 & -CH-ONO \\
\text{nitrosates} & \text{nitro-} & \text{. dinitro} & \text{dinitrites} \\
& \text{nitrites} & \text{compounds}
\end{array}
$$
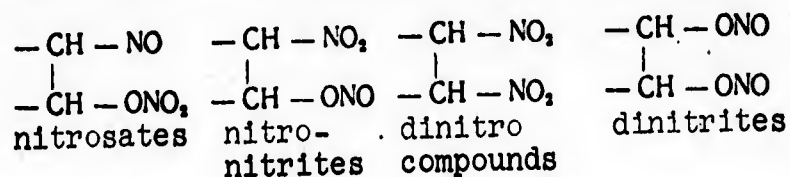
Only the dinitro compounds, of similar types of compounds, are stable. The remaining types of compounds are unstable, they are easily converted, and yield other reaction products. We can therefore anticipate that their formation will enhance the more intensive conversions which are important from the standpoint of the ignition of hydrocarbons with nitric acid.

Figure 165 shows the minimum hypergolic ignition temperature for a mixture of dicyclopentadiene and $\underline{n}$. decane with nitric acid, depending on the concentration of the dicyclopentadiene.

A temperature of 340° is required for the ignition of $\underline{n}$. decane with nitric acid, whereas a mixture of 25 and 35% dicyclopentadiene with decane ignites at 154 and 85°, respectively.

In a special investigation of the reaction between octadecene-1 and butadiene-1,3 with nitrogen tetroxide N_2O_4 in an ether solution at -10° and -30°, respectively, in order to clarify the formation of intermediate reaction products in the case of self-ignition [8], it was established that the reactions take place as follows:

$$
CH_3\,(CH_2)_{16} - CH = CH_2 + N_2O_4
\begin{array}{c}
\nearrow \quad CH_3\,(CH_2)_{16} \cdot CH\,(NO_2) - CH_2\,(NO_2) \\
\\
\searrow \quad CH_3\,(CH_2)_{16}CH - CH_2 \\
\qquad\qquad\quad | \quad\quad | \\
\qquad\qquad\quad ONO \quad NO_2
\end{array}
$$

- 470 -
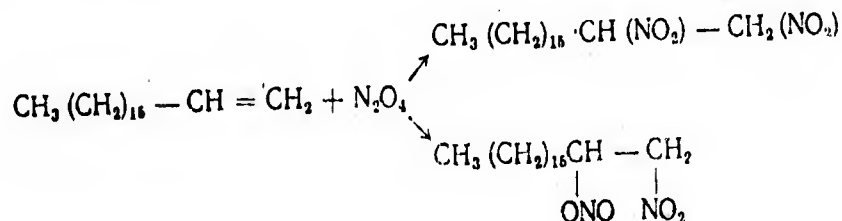
As a result of the reactions, 1,2-dinitrooctadecene and a combination product of the nitronitrite type are formed.
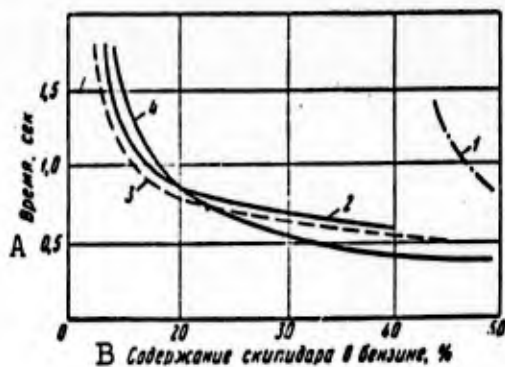
Fig. 166. Effect of additions of turpentine to gasoline on self-ignition with nitric acid and a mixture [melange].* 1) 96% HNO_3; 2) 95% HNO_3 with 15% oleum (fuming sulfuric acid); 3) 5% HNO_3 with 20% oleum; 4) 98% HNO_3 with 15% H_2SO_4. A) Time, sec; B) content of turpentine in gasoline, %.

Butadiene reacts with the oxides of nitrogen to form 1,4-dinitrobutene-2:

$$CH_2 = CH - CH = CH_2 + N_2O_4 \rightarrow \underset{NO_2}{CH_2} - CH = CH - \underset{NO_2}{CH_2}.$$
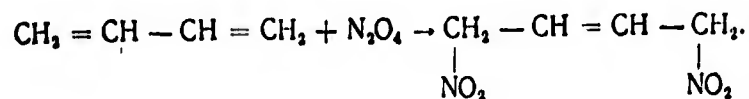
In connection with the high activity of the unsaturated compounds, the addition of these compounds to petroleum products may activate the self-ignition of the fuels (propellants) with nitric acid and in particular with melange [mixture]. Figure 166 presents data on the effect of an addition of turpentine on the ignition of gasoline with nitric acid and melange [mixture].

The basic part of the turpentine (up to 60-70%) consists of α-pinene — an unbranched bicyclical unsaturated hydrocarbon:

*see MS page 485

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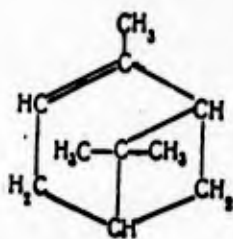
This hydrocarbon is hypergolic with nitric acid and in particular with melange [mixture].

The addition of turpentine may activate the ignition process of petroleum products, but not to such an extent as to make it possible to produce the hypergolic ignition of the propellant with a small period of induction.

3. Self-Ignition of Combustible Drops Falling into Nitric-Acid Vapors at High Temperatures

In other works [9] a study was undertaken of the hypergolic properties and the combustion of drops of a number of combustible substances, employed in the composition of rocket propellants, as they fall into nitric-acid vapors at high temperatures.

The investigation was carried out on a device such as that shown in Figs. 167 and 168. The device consists of a quartz reaction tube 4, heated by means of an electric coil to 300-600°. The reaction tube is filled with nitric-acid vapors which are formed in an acid-vapor generator 2 during boiling. The acid vapors are heated in a superheater 3 and enter into the reaction tube where the combustible drops, on coming into contact with the nitric-acid vapors at a temperature of 300-600°, ignite on their own and burn up.

The instant of drop separation is determined by a photoelectric cell 6. As the beam of the photocell is cut, the stopcock 5 is opened, as a result of which the drops fall into the reaction chamber.

The ignition and combustion of the drops is determined by means of high-speed photography (Fig. 169). The ignition of drops of triethyl-

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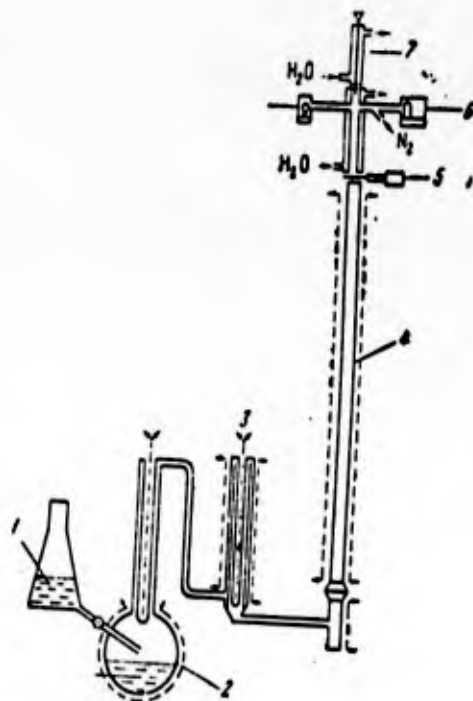
Fig. 167. Diagram of device used to study hypergolic properties of drops in nitric-acid vapors. 1) Flask with nitric acid; 2) nitric-acid evaporator; 3) nitric-acid vapor superheater; 4) quartz reaction tube; 5) stopcock; 6) photoelectric cell; 7) pipette with combustible.

amine takes place after 28.6 milliseconds. After 31.2 milliseconds, the combustion becomes intense.

Figure 170 shows the effect of the temperature of the nitric-acid vapors on the hypergolic ignition lag for combustible drops having a diameter of about 3-3.1 mm, said drops falling through the nitric-acid vapors. The composition of the initial acid is as follows: HNO_3, 98.08%; N_2O_4, 0.12%; and H_2O, 1.7%.

The temperature of the combustible is 19°. Figure 171 shows the effect of the initial propellant temperature on the hypergolic ignition lag.

The least ignition lag is exhibited by triethylamine, and this lag does not change in magnitude within a range of temperatures from

350 to 550°. Cyclohexene — a substance that is not hypergolic with nitric acid — produces the ignition of the drops at a temperature of around 475°, and the ignition lag changes markedly as a function of temperature. Allylamine occupies a middle position between triethylamine and cyclohexene, so that it reacts less vigorously with HNO_3, but more vigorously than the unsaturated hydrocarbons.

The hypergolic substances react with nitric-acid vapors at substantially lower temperatures than do the majority of the hydrocarbons (with the exception of the dienes). This represents the difference between the hypergolic and nonhypergolic combustibles under rocket-engine operating conditions; the process of ignition and combustion for nonhypergolic combustibles in ZhRD chambers requires a greater period of time than is needed for hypergolic combustibles. This is, on the whole, reflected in the stability of the combustion process in connection with a great induction period.

4. Concentration Limits, Combustion Temperature, and Normal Rate of Flame Propagation for Mixtures of Combustibles with Nitrogen Oxides

To conceive of the mechanism of propellant combustion in a ZhRD chamber we must know the concentration limits and the rates of flame propagation in the nitrogen oxide-hydrocarbon system. However, there are almost no data about this in the literature.

Below we present some of the limited data which are known in this area.

Figures 172-175 show the concentration limits for the propagation of flames produced by propellant mixtures consisting of nitrous oxide with such hydrocarbons as methane, propane, propylene, and butane, with various combinations of combustible mixtures and low pressures [10].

The nitrous oxide is an endothermic oxidizer, and the combustion of the hydrocarbons with N_2O can be presented by the following general
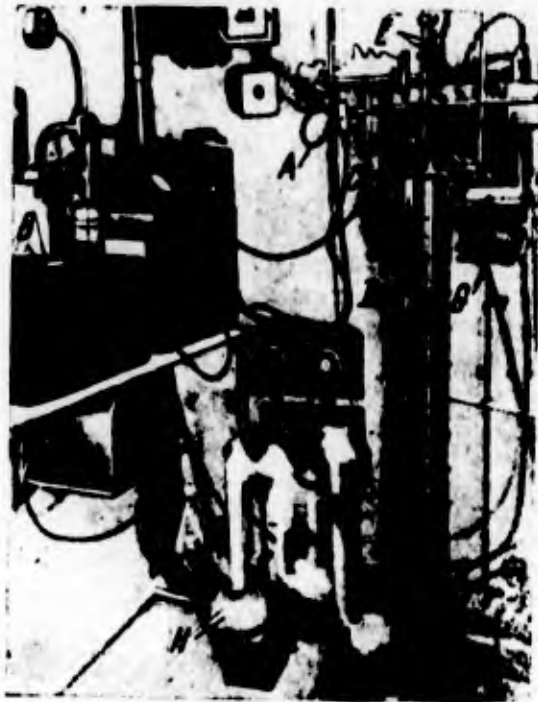
Fig. 168. General view of device used to
study the hypergolic properties of drops
falling into nitric-acid vapors. A) Pho-
tocell; B) oscillograph; C) stopcock; D)
heated quartz tube with oxidizer vapors;
E) dropper; F) light source; G) photo-
cell for recording of ignition; H) heater
(boiler) to produce nitric-acid vapors.

equation:

$$C_nH_{2n+2} + (3n + 1) N_2O \rightarrow nCO_2 + (n + 1) H_2O + (3n + 1) N_2.$$
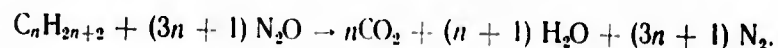
As the molecular weight of the hydrocarbons increases in the
transition from methane to butane, the ignition range is reduced, par-
ticularly toward the rich mixtures.

Normal rates of flame propagation for vapor-air rocket-propellant
mixtures are not presented in the literature. These data are known
only for the simplest of systems.

Adams [12] determined the normal rate of flame propagation for
mixtures consisting of $NO + H_2$, $N_2O_4 + H_2$, and $NH_3 + NO$, for which ex-
tremely varied normal rates of flame propagation were obtained for the
stoichiometric composition.

Table 123 presents the normal rates of flame propagation and com-
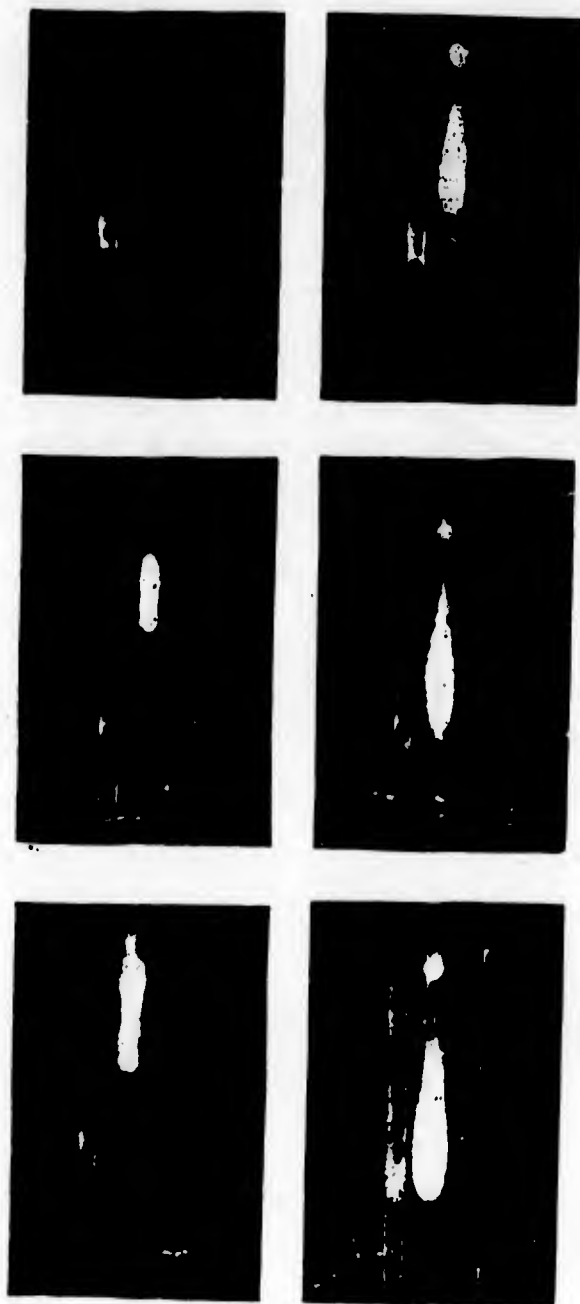
Fig. 169. High-speed photograph of self-ignition and combustion of triethylamine drops in nitric-acid vapors, during the following intervals: a) 28.6 milliseconds; b) 31.2 milliseconds; c) 31.9 milliseconds; d) 32.7 milliseconds; e) 33.4 milliseconds; f) 34.1 milliseconds.

bustion temperatures for several combustible mixtures.

The rate of flame propagation for combustible mixtures with nitrogen dioxide is substantially higher than in the case of nitrogen oxide.

In a study of the combustion of methane with nitrogen oxide, the
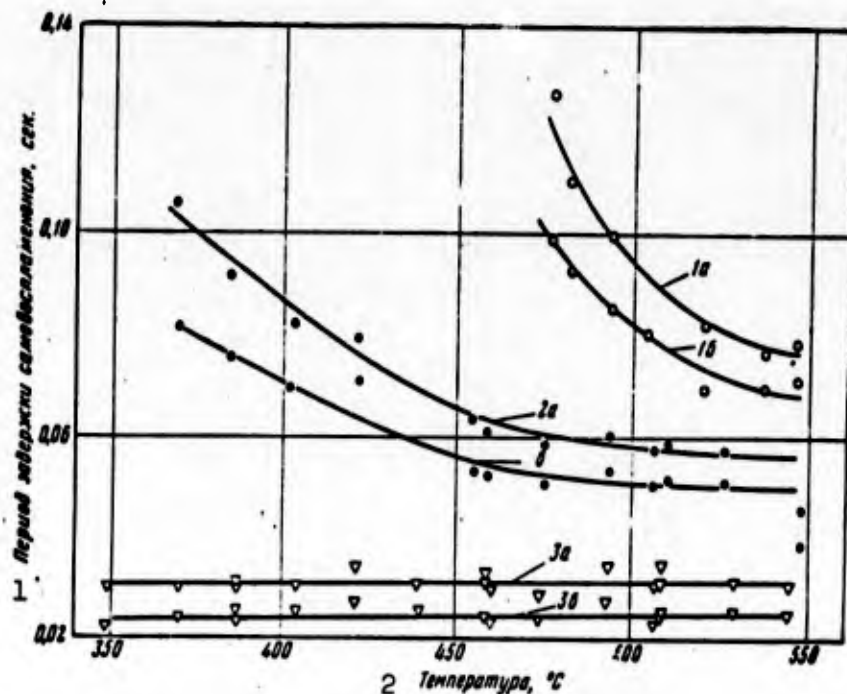
Fig. 170. Effect of temperature on self-ignition
lag for drops of cyclohexane, allylamine, and tri-
ethylamine, falling into nitric-acid vapors. a)
Ignition of vapor phase of drop; b) combustion of
drop; 1a and 1b) cyclohexene, drops $3.09 + 0.12$
mm; 2a and 2b) allylamine, drops $3.18 + 0.13$ mm;
3a and 3b) triethylamine, drops $3.00 + 0.14$ mm.
1) Hypergolic ignition lag, sec; 2) temperature, °C.

following lines were observed in the flame spectrum for CH_4 + NO: CH,
CN, NH, and OH, which indicates the presence of corresponding inter-
mediate reaction products [12-14].

5. Theoretical and Operational Parameters for a Kerosene-Nitric Acid Propellant

Similar data on the utilization of petroleum products together
with nitric acid as an oxidizer in rocket engines are not given. Only
in individual articles [6, 7] is the theoretical and practical possi-
bility of using petroleum products in rocket engines examined. These
articles describe a test stand with an engine chamber capable of de-
veloping 225 kg of thrust, and this device was employed to test pro-
pellants consisting of nitric acid and kerosene, with a chamber pres-
sure ranging from 20 to 40 kgf/cm^2.

Figure 176 shows the design of a combustion chamber of an experi-
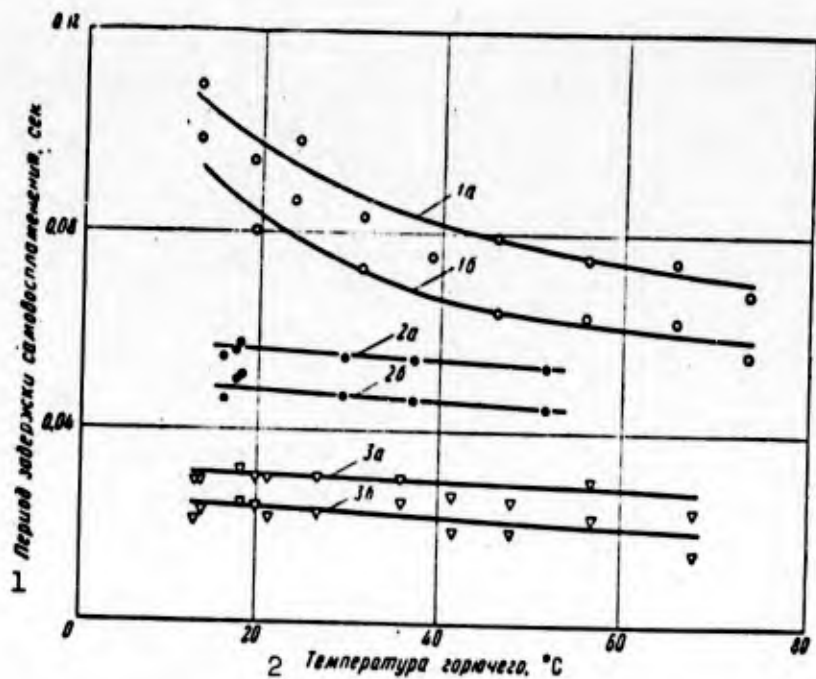
Fig. 171. Effect of initial propellant temperature on hypergolic ignition lag for drops of propellant (having dimensions 3.0-3.18 mm) falling into nitric-acid vapors at 475°. a) ignition of vapors of drops; b) combustion of drop; 1a and 1b) hypergolic ignition of cyclohexene drop; 2a and 2b) allylamine; 3a and 3b) triethylamine. 1) Hypergolic ignition lag, sec; 2) temperature of combustible, °C.

mental engine operating on nitric acid and kerosene.

Figure 177 considers the calculation (theoretical) specific-thrust characteristics of a propellant consisting of kerosene and nitric acid as a function of various weight ratios between the oxidizer and the combustible [1].

The specific thrust obtained experimentally with nitric acid and aviation kerosene, with an optimum oxidizer-to-combustible weight ratio of 4.5 and for various chamber pressures is presented below.

Pressure, atm	Specific impulse, sec
20	222
34	235
40.7	246

Figure 178 shows the results obtained from a determination of the effect, for the same propellant, of the composition of the propellant
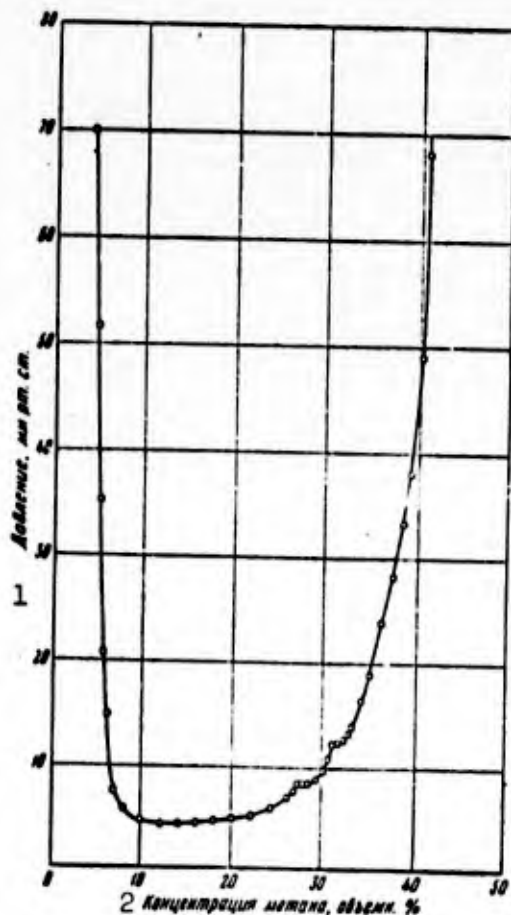
Fig. 172. Area of ignition of methane with nitrous oxide. 1) Pressure, mm Hg; 2) concentration of methane, % by volume.
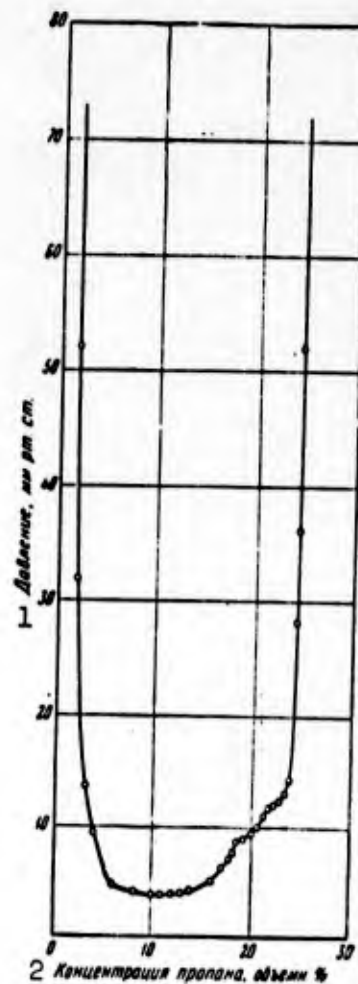
Fig. 173. Area of ignition of propane with nitrous oxide. 1) Pressure, mm Hg; 2) concentration of propane, % by volume.

TABLE 123

Normal Rate of Flame Propagation and Combustion Temperature for a Number of Combustibles with Oxides of Nitrogen [12-14]

1 Компоненты	Нормальная скорость распространения пламени, см/сек 2	Температура горения, °C 3	
		4 теоретическая	5 экспериментальная
$H_2 + NO$	30	2840	2820
$H_2 + \frac{1}{2}NO_2$	260	2660	2550
$NH_3 + 1\frac{1}{2}NO$	70	2675	2640
$C_2H_2 + 5NO$	—	3090	3095
$C_2H_2 + 7NO$	—	2855	—
$C_2H_6 + 7NO$	—	—	2865

1) Component; 2) normal rate of flame propagation, cm/sec; 3) combustion temperature, °C; 4) theoretical; 5) experimental.

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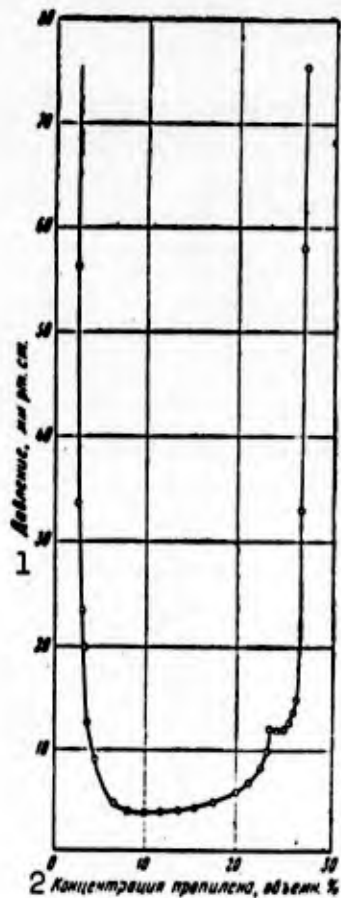
Fig. 174. Area of propylene ignition with nitrous oxide. 1) Pressure, mm Hg; 2) concentration of propylene, % by volume.
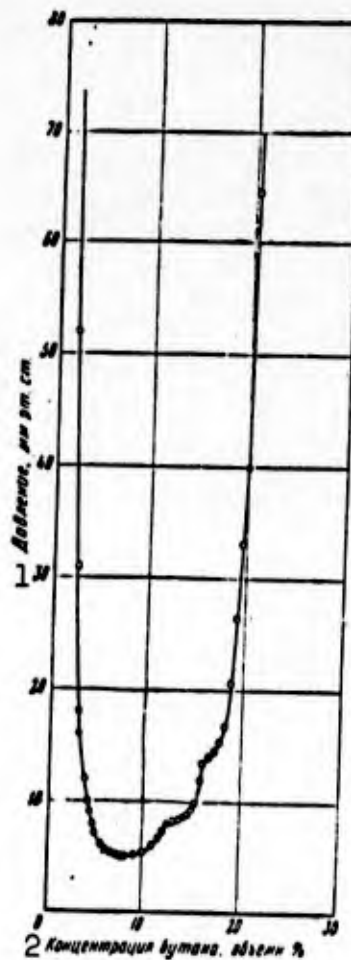
Fig. 175. Area of butane ignition with nitrous oxide. 1) Pressure, mm Hg; 2) concentration of butane, % by volume.

mixture on specific thrust with a combustion-chamber pressure of 40.7 atm. The greatest specific thrust is developed at $\alpha = 0.85$.*

Aviation kerosenes of the JP-3 and JP-4 types are employed as combustibles with nitric acid; these kerosenes are saturated. However, these combustibles, as was demonstrated above, are not too active and this has a negative effect on engine operation.

Pyrolysis products exhibit greater chemical activity in ZhRD, since these contain a significant quantity of unsaturated hydrocarbons; it is for this reason that the USA developed a special combustible based on products of pyrolysis, which is known as "HF-D." This combus-
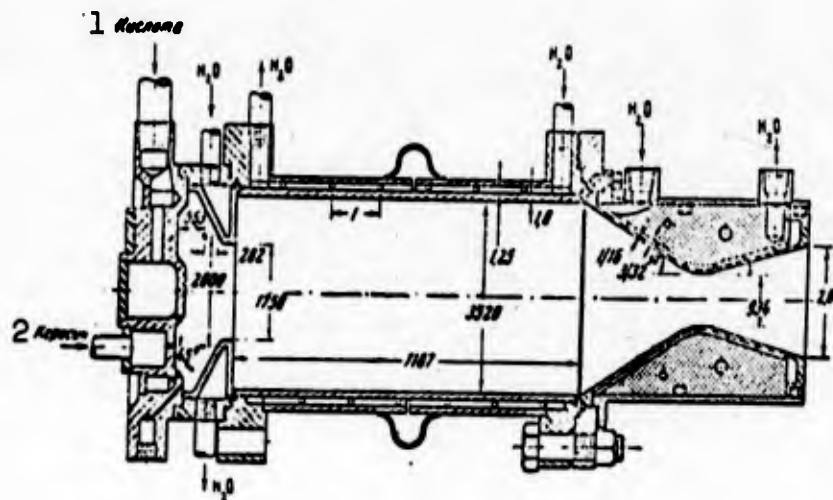
Fig. 176. Design of ZhRD combustion chamber operating on kerosene and nitric acid to produce 220 kg of thrust (dimensions given in inches). 1) Acid; 2) kerosene.
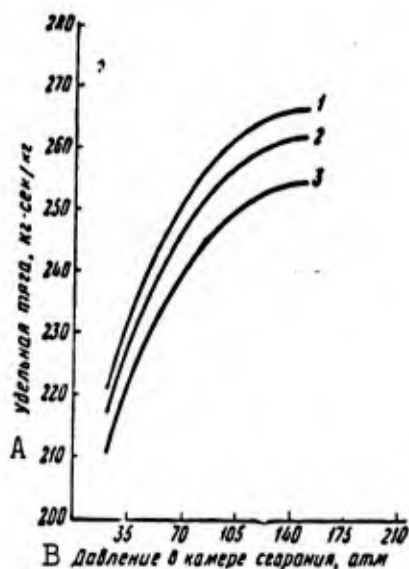
Fig. 177. Effect of propellant composition (weight ratio of oxidizer to combustible) and pressure in combustion chamber on specific thrust (specific impulse), obtained with a kerosene-nitric acid propellant. 1) Oxidizer-to-combustible ratio — 4.8; 2) 5.53; 3) 6.32. A) Specific thrust, kg·sec/kg; B) pressure in combustion chamber, atm.

tible has the following characteristics:

Fractional composition:

start of boiling................ −122°

50% distilled at temperature.... −165°

end of boiling.................. −220°

Specific weight................... 0.94

Freezing point not above.......... −73°

Viscosity at 21° not above........ −1.71 centistokes

The "HF-D" combustible burns better than the JP-4 gas-turbine fuel.
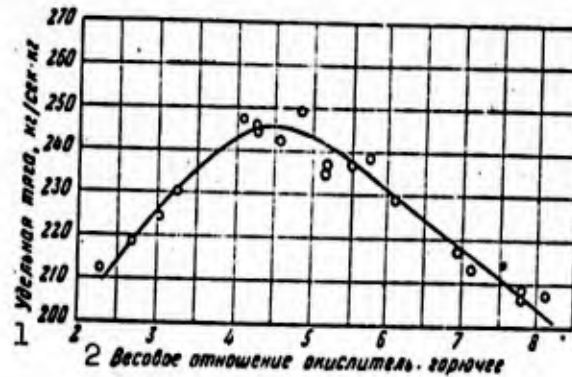
Fig. 178. Effect of oxidizer (nitric acid)-to-combustible (kerosene) weight ratio on specific thrust at a chamber pressure of 40.7 atm. 1) Specific thrust, kg/sec·kg; 2) oxidizer-to-combustible weight ratio.

TABLE 124

Energy Characteristics for Kerosene-, Nitric Acid-, and Nitrogen Oxide-Based Fuels [16]

1 Окислитель	2 Удельный импульс (сек.) при давлении					
	20 am	30 am	40 am	50 am	60 am	80 am 3
4 Азотная кислота 98%-ная	226	237	244	247	253	260
5 Азотной кислоты 80% 6 Окислов азота 20%	228	238	244	250	254	262
7 Азотной кислоты 60% 8 Окислов азота 40%	230	245	249	255	260	265

1) Oxidizer; 2) specific impulse (sec) at pressures of; 3) atm; 4) 98% nitric acid; 5) 80% nitric acid; 6) 20% nitrogen oxide; 7) 60% nitric acid; 8) 40% nitrogen oxides.

We know of propellants for rocket engines that have been derived

from coaltars. Monocyclical and polycyclical aromatic hydrocarbons are contained in the tar, as are monatomic and biatomic phenols.

We also know of reaction (jet)-engine combustibles derived from shale tars.

Table 124 presents the energy characteristics of propellants based on kerosene, nitric acid, and nitrogen oxides (Table 124).

Nitric acid with nitrogen oxides is a more perfect oxidizer than 98% nitric acid.

In the USA, 98% nitric acid was replaced for anti-aircraft rockets by an oxidizer consisting of 80% nitric acid and 20% nitrogen oxides [15]. This was a result of the need to increase the stability of the oxidizer, since the 98% nitric acid loses oxygen during storage, and this oxygen is needed in order to develop a higher pressure in the tanks.

The utilization of an oxidizer consisting of 20% N_2O_4 and 80% HNO_3 results in an increase in specific impulse by 2 to 3 units.

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Manu- script Page No.	[Footnote]
480	Weight ratio, 4.5.
485	Melange refers to a mixture containing at least 87% HNO_3 and and 7·5% H_2SO_4 (generally, about 10%).

Chapter 6

FUELS BASED ON CONCENTRATED HYDROGEN PEROXIDE

Concentrated hydrogen peroxide (concentration 80-90%) has come into use as an auxiliary fuel in liquid reaction-thrust engines (to drive turbopumps) and as a monopropellant fuel for aviation starter engines, and was used earlier (in Germany) as an oxidant for jet-propulsion fuels.

Hydrogen peroxide has been used in the following objects [1]:

1) rocket-propelled interceptors;

2) guided aerial torpedoes;

3) starting devices for launching winged missiles;

4) booster engines to assist aircraft in taking off;

5) marine torpedoes;

6) the turbines and turbopumps that feed fuel into rocket engines.

And, finally, concentrated hydrogen peroxide is used as a source of oxygen in the submarine fleet.

During 1942-1945, concentrated hydrogen peroxide was used in liquid-fuel rocket engines in combination with hypergolic combustibles.

The nature of the reactions of hydrogen peroxide with a number of combustible substances is shown in Table 125.

The reactions of hypergolic combustibles with hydrogen peroxide are promoted by catalysts, including salts of iron, copper and vanadium.

Hydrazine hydrate self-ignites well with hydrogen peroxide. Among organic materials, certain alcohols, aldehydes, and ketones also self-ignite in the presence of catalysts. Amines do not self-ignite as well

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as alcohols and ketones. In this respect, hydrogen peroxide differs as an oxidant from nitric acid.

Two typical combustible compositions have been used [2] as self-igniting combustibles with concentrated hydrogen peroxide (87%).

The first recipe is based on methyl alcohol and hydrazine:

I. Methyl alcohol.................... 57%
   Hydrazine hydrate................ 30%
   Water............................ 13%
   Catalyst — potassium copper cy-
   anide $K_3Cu(CN)_4$.............. 0.24%
   Heating value.................... 1020 kcal/kg
   Specific impulse (at 20 atm)..... 180 sec

Hydrazine was of interest as a combustible in fuels based on hydrogen peroxide and is now attracting attention as a combustible for fuels based on other oxidizers.

Hydrazine is a substance with a high melting point of $+2^o$ and a boiling point of 114°. With alcohols (methyl, ethyl, etc.), hydrazine forms low-freezing mixtures [3]:

	Freezing point, ^{o}C
$N_2H_4 \cdot CH_3OH$	—47,3
$N_2H_4 \cdot 2CH_3OH$	—57,8
$N_2H_4 \cdot 4CH_3OH$	—69,5
$N_2H_4 \cdot C_2H_5OH$	—31,2

Figures 179 and 180 show the phase diagrams for the N_2H_4-CH_3OH and N_2H_4-C_2H_5OH systems as functions of composition.

Hydrazine hydrate $N_2H_4 \cdot H_2O$ has a melting point lower than that of hydrazine, i.e., $—40^o$; its boiling point is $+119^o$.

A recent development is the "AR" hydrogen-peroxide liquid rocket engine, which was designed for use on "FI-4" pursuit-interceptors, which take off from the decks of ships in the US Navy [4]. In the middle of 1959, several modifications of the "AR" engine were built to operate on 90% hydrogen peroxide and a jet combustible of the type of

TABLE 125

Nature of Reactions of Certain Combustibles Diluted with Equal Quantities of Acetone with Concentrated Hydrogen Peroxide [2]

Combustible	Nature of reaction in presence of catalyst	
	$V_2O_2Cl_4 \cdot 5H_2O$	$CuCl_2 \cdot 2H_2O$
Triethylamine............:	Reaction without ignition	
Butylamine.................	Reaction	Ignition with time delay
Triethanolamine.............	"	Ignition
Aniline.....................	"	Ignition with delay
Xylidine...................	Ignition with time delay	Ignition
Cyclohexylamine.............	Reaction	Ignition with delay
Hydrazine hydrate...........	Ignition	Ignition
Methyl alcohol..............	Reaction	Reaction
Ethyl alcohol...............	"	"
Isopropyl alcohol...........	Vigorous reaction	"
Isobutyl alcohol............	Ignition with delay	
Isoamyl alcohol.............	Same	
Tetrahydrofurfuryl alcohol..	Ignition	Ignition
Furfuryl alcohol............	"	"
Allyl alcohol...............	"	Ignition with delay
Benzaldehyde................	"	Ignition
Cinnamic aldehyde...........	"	"
Furfurol....................	"	"
Acetone.....................	Vigorous reaction	
Octylene....................	Ignition with delay	Reaction
Benzene.....................	Does not react	—
Cyclohexane,................	" " "	—

JP-4 or JP-5 kerosene.

The thrust of the AR-2 engine is controllable between 1360 and 2720 kg at an altitude of 10.7 km. It burns for three minutes, weighs 104 kg, and is 800 mm long. Other modifications of the engine — the AR-2-1 and AR-2-2 — work for seven minutes; these engines are 1440 mm long. The combustible is used to cool the engine; its combustion tem-
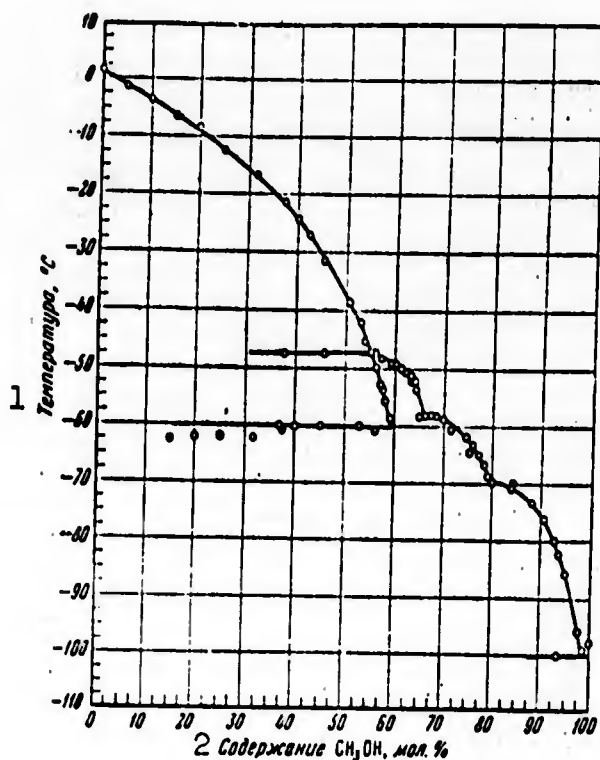
Fig. 179. Diagram of state of N_2H_4–
–CH_3OH system. 1) Temperature, °C;
2) CH_3OH content, mole %.

perature is 2700° and the pressure is 35-42 atm, depending on the thrust.

A silver-coated metallic screen 230 mm in diameter is used as a catalyst for decomposition of the hydrogen peroxide. The hydrogen peroxide is stored in a fuel tank with a capacity of 1140 liters, the consumption of oxidizer is 380 liters/min, and the weight ratio between the oxidizer and the combustible is 7:1.

In 1959, more than 100 flights were made by an interceptor equipped with this engine. Over 104 minutes of operating time were logged. Plans for further refinement call for increasing the thrust of the engine to 5500 kg.

Another type of combustible used in conjunction with hydrogen peroxide includes combustibles containing monobasic phenols [2]:

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II. Raw pyrocatechol................. 30%
    Methyl alcohol.................. 62.5%
    Catalyst $K_3Cu(CN)_4$............. 7.5%
    Heating value.................. 1100 kcal/kg
    Specific impulse............... 180-183 sec

The combustible self-ignites with concentrated hydrogen peroxide, with a short time delay. In ten experiments, the delay time of self-ignition was determined to range between 0.014 and 0.033 sec. The average self-ignition delay was 0.024 sec.

Table 126 presents theoretical characteristics of fuel mixtures based on hydrogen peroxide and a number of combustibles.
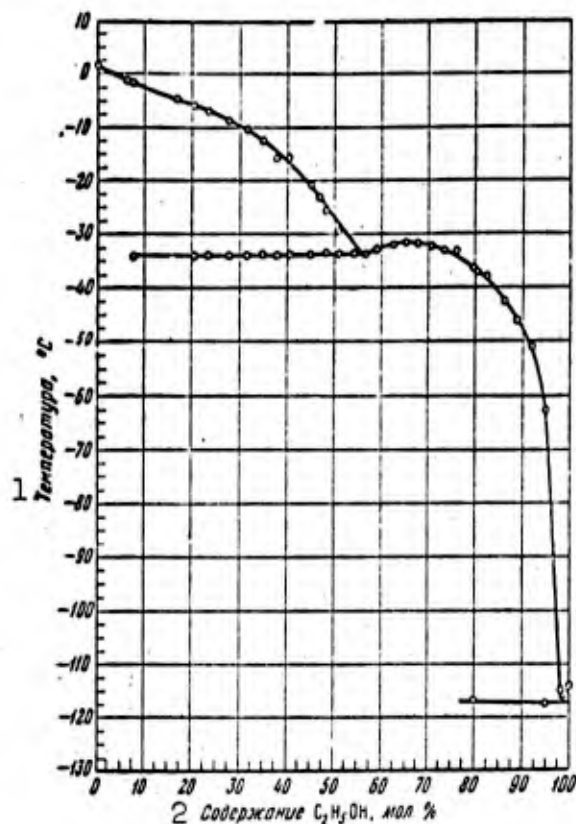
Fig. 180. Diagram of state of N_2H_4— —C_2H_5OH system. 1) Temperature, $^{\circ}C$; 2) C_2H_5OH content, mole-%.

Fuels consisting of 90% hydrogen peroxide with kerosene have energy data close to those of fuels based on nitric acid, although they are somewhat inferior to the latter as regards specific impulse and

TABLE 126

Theoretical Characteristics of Fuels Based on Hydrogen Peroxide [2]*

1 Концентрация перекиси водорода, %	2 Горючее	3 Отношение окислителя к горючему	4 Плотность топлива	5 Температура горения, °C	6 Скорость истечения, м/сек	7 Удельный импульс, сек
100	8 Гидразин	1,45	1,23	2450	2420	247
100	9 Керосин	5,75	1,28	2580	2300	233
100	10 (Этиловый спирт 92,5%-ный)	3,40	1,22	2440	2250	220
100	11 Нитрометан	0,67	1,27	2690	2230	227
87		1,00	1,28	2550	2250	229
87	12 Метиловый спирт	3,70	1,19	2280	2210	225
87		5,70	1,24	1038	1960	199

*At a chamber pressure of 21 atm.

1) Hydrogen peroxide concentration, %; 2) combustible; 3) ratio of oxidizer to combustible; 4) density of fuel; 5) combustion temperature, °C; 6) outflow speed, m/sec; 7) specific impulse, sec; 8) hydrazine; 9) kerosene; 10) (ethyl alcohol, 92.5%); 11) nitromethane; 12) methyl alcohol.

specific gravity. To secure stable combustion of fuels based on hydrocarbons and hydrogen peroxide, it has been proposed that the peroxide first be catalytically decomposed so that the combustion process will take place in heated decomposition products [4, 5].

TABLE 127

Theoretical Characteristics for Hydrogen Peroxide as a Monopropellant Fuel* [4]

1 Концентрация перекиси водорода, %	2 Теплопроизводительность, ккал/кг	3 Температура продуктов разложения, °C	4 Скорость истечения, м/сек	5 Удельный импульс, сек
100	394	975	1430	145
90	296	738	1300	131
80	185	580	—	90

*Chamber pressure 21 atm.

1) Hydrogen peroxide concentration, %; 2) heating value, kcal/kg; 3) temperature of decomposition products, °C; 4) outflow speed, m/sec; 5) specific impulse, sec.

TABLE 128

Density and Viscosity of Concentrated Solutions of Calcium Permanganate [6]

1 Концентрация иона MnO$_4^-$, %	2 Плотность			3 Вязкость, сантипаузы		
	10°	25°	40°	10°	25°	40°
20	1,209	1,201	1,187	1,667	1,181	0,886
30	1,347	1,336	1,324	1,704	1,542	1,175
40	1,506	1,493	1,479	3,230	2,310	1,877
52	1,750	1,734	1,719	9,360	6,270	4,520

1) Concentration of MnO$_4^-$ ion, %; 2) density;
3) viscosity, centipoises.

It appears that hydrogen peroxide will not be used to any signifi-
cant extent in the future as an oxidant for bipropellant fuels. How-
ever, concentrated hydrogen peroxide can be used as a single-component
fuel. In this case, the hydrogen peroxide is decomposed with evolution
of a large quantity of gases that have been heated to high temperature.
But the specific impulse that results is considerably smaller than that
available from ordinary rocket fuels (Table 127).

The properties of the decomposition products of 90% hydrogen per-
oxide are listed below:

Heating value......................... 617 kcal/kg
Temperature of gases................. 730°
Volume of gases...................... 1700 liters/kg
Partial volume of O$_2$................ 0.2994 mole
Partial volume of H$_2$O.............. 0.7076 mole
O$_2$ content in gaseous mixture....... 42.3 % by weight

Figure 181 shows the most important characteristics of H$_2$O$_2$ as
functions of concentration. It will be seen from these characteristics
that at a 64.5% H$_2$O$_2$ concentration, so much heat is evolved that the
entire solution is vaporized at 100°; at an 80% concentration, the
H$_2$O$_2$ gives a vapor-gas mixture with a temperature of 460°, while 100%
H$_2$O$_2$ gives a vapor-gas mixture heated to 950°.

Figure 182 presents a temperature-enthalpy diagram showing the final decomposition temperature as a function of the H_2O_2 concentration and the pressure $\underline{p}$.

Hydrogen peroxide is used as a monopropellant fuel in combination with aqueous solutions of calcium or sodium permanganate as a catalyst. Such a fuel was used for the "Focke-Wulf" and "Heinkel" aircraft, whose engines developed thrusts of 300, 500, and 1000 kg, and in the starting devices for winged missiles.

TABLE 129

Freezing Point of Aqueous Solutions of Calcium and Sodium Permanganates [6]

1 Концентрация иона MnO_4^-, %	2 Температура замерзания раствора, °C	
	$Ca(MnO_4)_2 \cdot H_2O$	$NaMnO_4 \cdot 3H_2O$
5	—1	—
15	—4,5	—
25	—10	— 9
35	—22	—
41	—	—15
42	—37	—
45	—53	—
52	—49	—

1) Concentration of MnO_4^- ion, %; 2) freezing point of solution, °C.

In these systems, catalytic decomposition of hydrogen peroxide is effected with H_2O_2 and a concentrated solution of $NaMnO_4$ or $Ca(MnO_4)_2$ fed simultaneously into the chamber of the liquid rocket engine. The reaction begins quickly with a smooth rise in pressure to 50-70 kgf/cm^2 in 0.01-0.02 sec. The catalyst contains 40-50% of the ion MnO_4^- in aqueous solution and is taken in quantities of about 5-6% to the hydrogen peroxide. The catalyst must enter the reaction chamber slightly in advance.
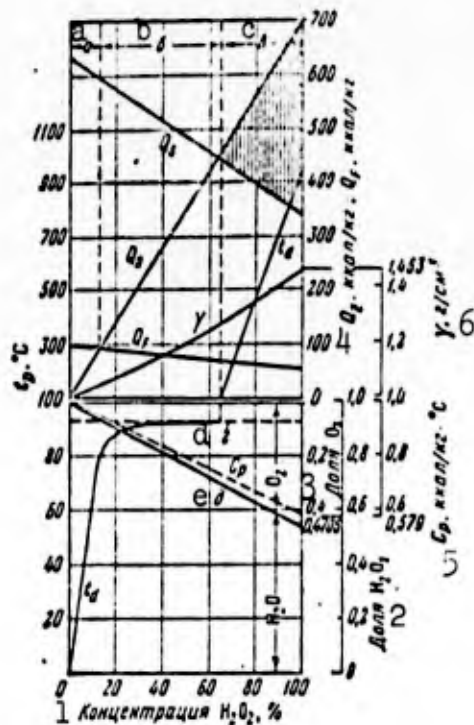
Fig. 181. Vapor temperature t_D and physical parameters as functions of concentrations of H_2O_2 solution at pressure of 1 atm and initial temperature of 0^0. a,b,c) Region of liquid phase, wet vapor and super-heated vapor; d) temperature level at which complete evaporation takes place; e) curve of oxygen content. 1) H_2O_2 concentration, %; 2) fraction of H_2O_2; 3) fraction of O_2; 4) Q_z, kcal/kg; Q_f, kcal/kg; 5) C_p, kcal/kg·^{0}C; 6) γ, g/cm^3.

Thus, a necessary component for a fuel of this type is the permanganate solution, which can be replaced by a solid catalyst inserted into the combustion chamber.

It is appropriate to list the physicochemical properties of permanganate solutions in connection with their use in rocket engines (Figs. 183 and 184; Tables 128 and 129).

Figure 184 shows the freezing temperatures of calcium permanganate solutions as functions of concentration.
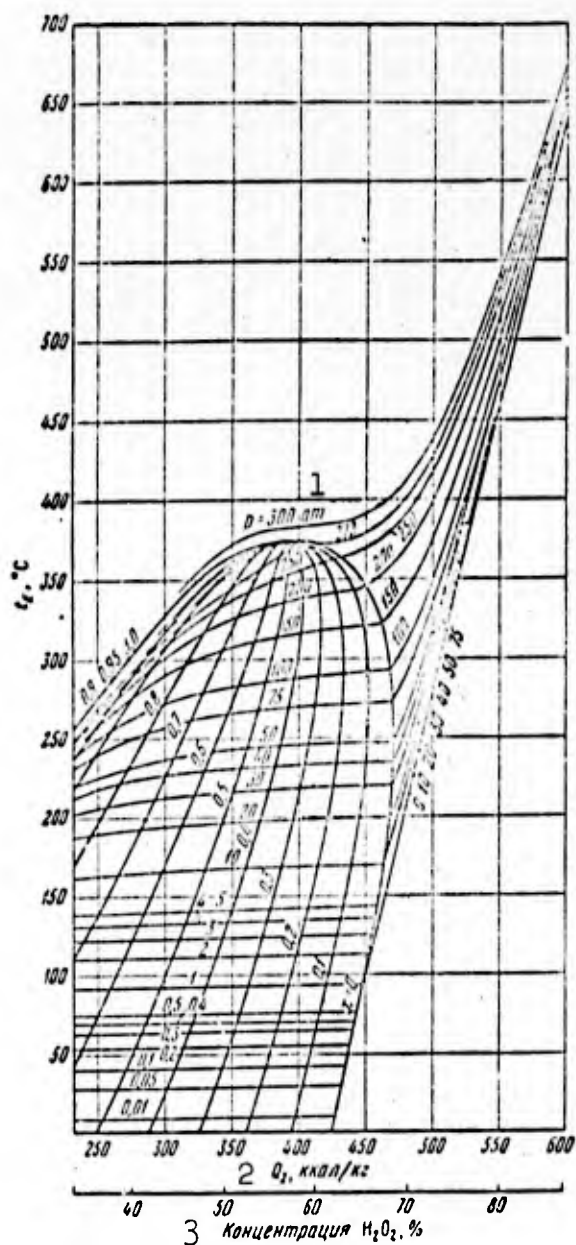
Fig. 182. Final decomposition temperature t_E and moisture content $\underline{x}$ of H_2O_2 solution as a function of heat of decomposition Q_Z and the concentration of H_2O_2 at various pressures and an initial temperature of $0°$. 1) atm; 2) Q_Z, kcal/kg; 3) H_2O_2 concentration, %.

Special measures are required in technical use of such unusual permanganate solutions. Thus, for example, these solutions liberate oxygen quite readily and can ignite many organic materials.

"Summer" and "winter" permanganates were used in Germany [1].
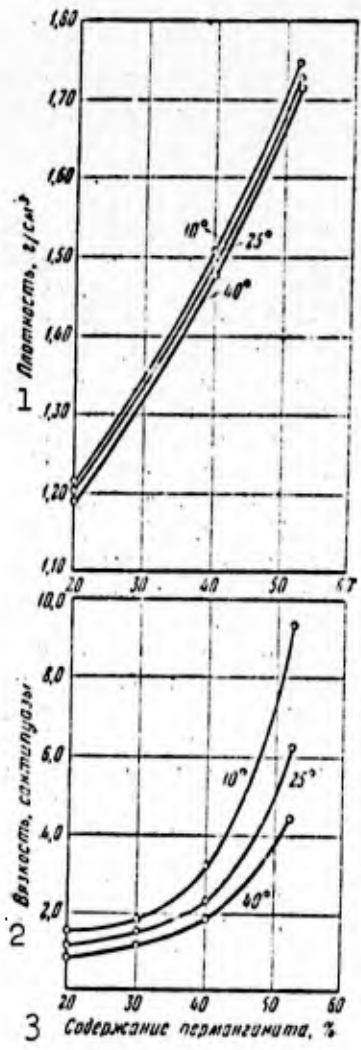
Fig. 183. Density and viscosity of calcium permanganate solutions. 1) Density, g/cm^3; 2) viscosity, centipoises; 3) permanganate content, %.
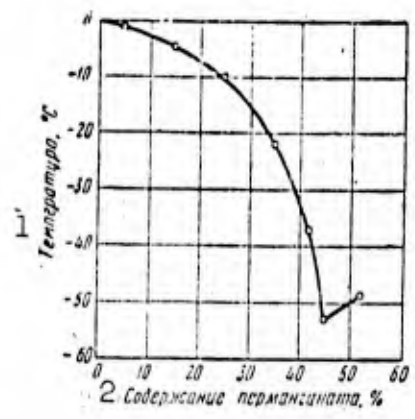
Fig. 184. Freezing point of aqueous solutions of calcium permanganate as a function of Ca(MnO$_4$)$_2$ concentration. 1) Temperature, °C; 2) permanganate content, %.
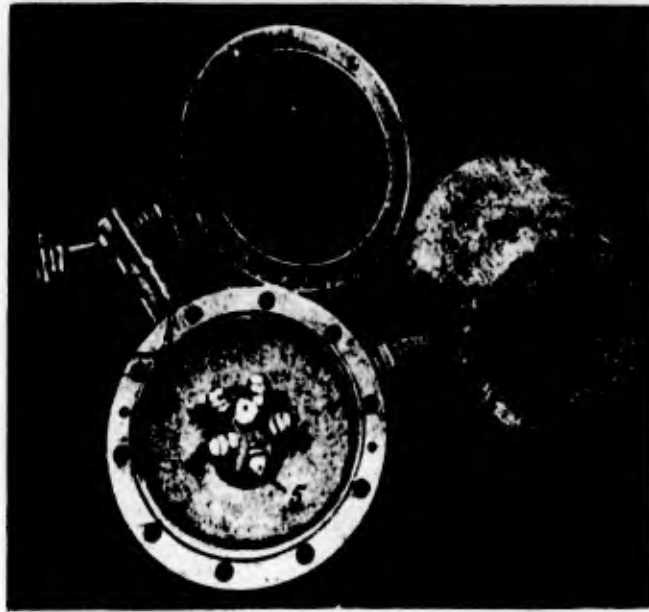
Fig. 185. Gas-generator chamber of Walter engine. 1) Steel housing; 2) bracket; 3) gas-exit tube; 4) cover; 5) injector nozzles; 6) pipeline for hydrogen-peroxide feed; 7) catalyst carrier; 8) perforated plate.
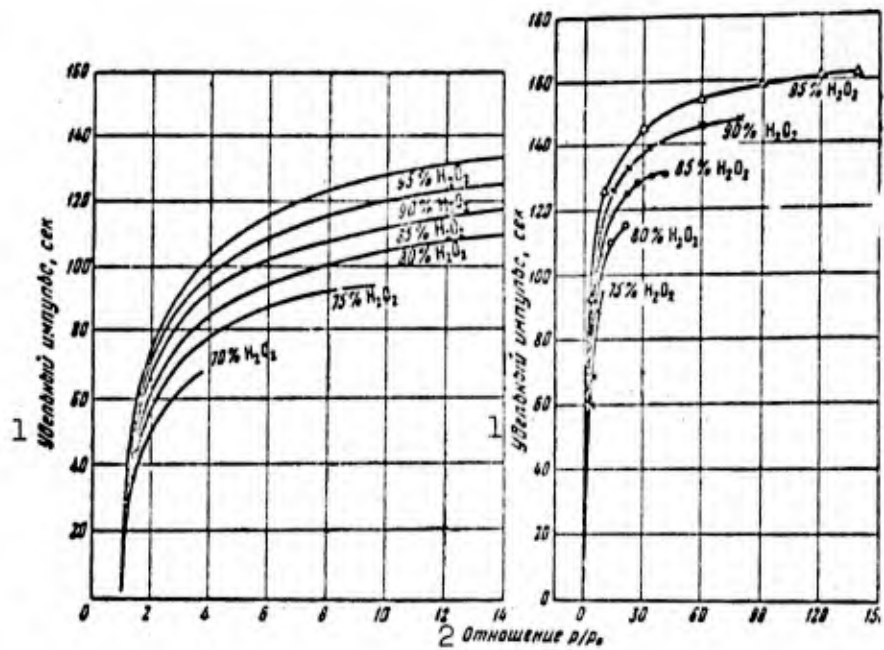
Fig. 186. Influence of H_2O_2 concentration and chamber pressure on specific thrust produced in catalytic decomposition of hydrogen peroxide. p) Chamber pressure; p_0) pressure at nozzle exit section.

1) Specific impulse, sec; 2) p/p_0 ratio.

Sodium permanganate could be used in summer. But its low solubility and the resulting high freezing points of the solutions did not permit its use in winter. Under winter conditions, therefore, the more soluble and lower-freezing calcium permanganate was used, e.g., in the following composition:

$$
\begin{aligned}
&\text{Ca(MnO}_4)_2 \ldots \ldots \ldots \ldots 38,6\% \\
&\text{NaMnO}_4 \ldots \ldots \ldots \ldots 1,75\% \\
&\text{Mg} \ldots \ldots \ldots \ldots \text{Следы 1} \\
&\text{K} \ldots \ldots \ldots \ldots \text{Нет 2} \\
&3 \ \text{Плотность (24°)} \ldots \ldots 1,406 \\
&\text{pH} \ldots \ldots \ldots \ldots 4,91 \\
&4 \ \text{Температура замерзания} \ldots -20°
\end{aligned}
$$

1) Traces; 2) none; 3) density
(24°); 4) freezing point.

Concentrated hydrogen peroxide is used to drive fuel-feeding turbopumps [7]. Catalytic decomposition of H_2O_2 results in a vapor-gas mixture that drives the turbine.

Catalytic decomposition of hydrogen peroxide takes place in a special gas generator which has a chamber filled with a solid catalyst, such as fragments of cement, porcelain or some other silicate material impregnated with permanganates. The catalyst must have mechanical strength and high activity over the entire operating period.

Figure 185 shows a chamber for decomposition of hydrogen peroxide as used in the Walter gas-generator motor, which operates on hydrogen peroxide [8].

The auxiliary gas-generator motor developed 90 hp. The motor was designed to feed oxidizer (hydrogen peroxide) and combustible (alcohol-hydrazine) into the combustion chamber of the main liquid rocket engine, which develops a thrust of 1700 kg. The Walter engine was installed on interceptors [9].

Figure 186 shows the influence of H_2O_2 concentration and combustion-chamber pressure on the specific impulse developed in catalytic

decomposition of hydrogen peroxide [10].

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Chapter 7

FUELS BASED ON LIQUID OXYGEN, OZONE, AND FLUORINE

Fuels based on liquid oxygen are distinguished by high heating values and high energy indicators. As a result, they have come into use in long-range rockets.

Ozone and fluorine and its compounds can be used as oxidants for rocket combustibles. Table 130 shows the physicochemical properties of the oxidizers listed.

TABLE 130

Physicochemical Properties of
Certain Rocket Oxidizers

1 Окислитель	2 Т. пл., °C	3 Т. кип., °C	4 Плотность при температуре кипения
5 Кислород . . .	—219	—183	1,14
6 Озон	—251	—111,1	1,46
7 Фтор	—223	—187	1,51
8 Окись фтора .	—224	—145	1,53
9 Трехфтористый хлор	— 82,6	÷ 11,7	1,77
10 Перхлорилфторид	—146	— 46,8	1,392
11 Тетрафторгидразин	—	— 73	—

1) Oxidizer; 2) melting point, °C; 3) boiling point, °C; 4) density at boiling point; 5) oxygen; 6) ozone; 7) fluorine; 8) fluorine oxide; 9) chlorine trifluoride; 10) perchloryl fluoride; 11) tetrafluorohydrazine.

As we have already noted, liquid oxygen is the basic form of oxidizer for long-range rockets. The combustible components used with such oxygen-base fuels are alcohols and hydrocarbon mixtures.

Alcohols containing varying quantities of water were first used for this purpose. Such a composition of the rocket fuel ensures favorable conditions for cooling the walls of the engine by the combustible component of the fuel, while a lower temperature is developed in the engine's combustion chamber than is the case with combustion of a fuel consisting of hydrocarbons and oxygen.

Theoretical characteristics for liquid-oxygen-based fuels are listed in Table 131.

Nitrogen-containing combustibles (ammonia and hydrazine), used with oxygen, provide a fuel distinguished by a higher specific thrust than the hydrocarbon-based fuels, but a lower combustion temperature.

A liquid-hydrogen/liquid-oxygen fuel gives the highest specific thrust, but has a low density (0.33).

Recently, ever-increasing attention has been devoted to hydrazine and its homologs (methyl hydrazine and dimethyl hydrazine). The properties of these compounds were dexcribed in Chapter 4 (Part Two).

Hydrazine is an extremely active combustible. The ignition range of hydrazine vapor with oxygen is extremely wide; this is accounted for by the endothermic nature and high chemical activity of hydrazine.*

Nitrogen-containing combustibles are more efficient than kerosenes, as will be evident from the following example:

1 Горючее	2 Плотность топлива	3 Удельный импульс $(p/p_1 = 50)$, сек.
1. Керосин	1,02	300
2. $N_2H_4 - 50\%$ . . . . $H_2N_2 (CH_3)_2 - 50\%$	1,02	312
3. $H_2N_2 (CH_3)_3 - 60\%$ . . . . $NH (C_2H_4NH_2)_2 - 40\%$	1,02	306
4. $H_2N_2 (CH_3)_2$	0,98	310
5. N_2H_4	1,07	313
6. NH_3	0,89	294

1) Combustible; 2) density of fuel; 3) specific impulse $(p/p_0 = 50)$, sec.

TABLE 131

Theoretical Characteristics of Oxygen-Based Fuels*
[1-4]

1 Топливо	2 Плотность топлива при 20°	3 Отношение окислитель: горючее	4 Коэффициент избытка окислителя	5 Теплопроизводительность, ккал/кг	6 Скорость истечения, м/сек	7 Удельный импульс, сек	8 Температура горения, °C
9 Кислород + водород . . .	0,330	3,00	0,85	—	3523	255	2366
10 Кислород + аммиак . . .	0,980	1,40	1	1660	2500	358	2733
11 Кислород + гидразин . .	1,090	0,57	1	—	2620	267	—
12 Кислород + гидразин .	1,050	0,50	0,83	—	2540	259	2480
13 Кислород + гидразин. . .	—	0,33	0,63	—	2414	246	—
14 Кислород + 100%-ный этиловый спирт	0,966	1,50	0,89	2020	2340	243	2910
15 Кислород + 95%-ный этиловый спирт	0,998	—	—	1970	2420	—	—
16 Кислород + 75%-ный этиловый спирт	0,994	1,30	—	1760	2310	239	2770
17 Кислород + 100%-ный метиловый спирт	0,895	1,25	0,92	1870	2300	238	2860
18 Кислород + метан	—	3,00	—	—	2460	255	2750
19 Кислород + газолин. . .	0,985	2,50	0,92	2270	2340	242	3000
20 Кислород + бензин . . .	—	1,56	—	—	2280	244	2240
21 Кислород + метиламин. .	0,985	2,00	—	—	2600	266	3060
22 Кислород + нитрометан	1,1390	0,08	—	—	2220	225	2590
23 Озон + толуол.	—	—	—	—	2820	265	2705

*With a combustion-chamber pressure of 21 atm and expansion of the combustion products to 1 atm.

1) Fuel; 2) density of fuel at 20°; 3) oxidant:
:combustible ratio; 4) excess-oxidant ratio; 5)
heating yield, kcal/kg; 6) outflow speed, m/sec;
7) specific impulse, sec; 8) combustion tempera-
ture, °C; 9) oxygen + hydrogen; 10) oxygen + am-
monia; 11) oxygen + hydrazine; 12) oxygen + hy-
drazine; 13) oxygen + hydrazine; 14) oxygen + 100%
ethyl alcohol; 15) oxygen + 95% ethyl alcohol; 16)
oxygen + 75% ethyl alcohol; 17) oxygen + 100%
methyl alcohol; 18) oxygen + methane; 19) oxygen +
+ gasoline; 20) oxygen + benzene; 21) oxygen +
+ methyl amine; 22) oxygen + nitromethane; 23)
ozone + toluene.

The second combustible, No. 2, which is known as aerozine, has
superior indices.

According to data of the theoretical rocket-fuels division of
"North American," rocket fuels based on liquid oxygen have the charac-
teristics indicated in Table 132.

In recent years, JP-4 gas-turbine kerosene has been replaced by a

TABLE 132

Characteristics of Liquid Rocket Fuels Based on Oxygen and Ozone

1 Топливо	2 Весовое отношение окислителя к горючему	3 Плотность при 27°	4 Удельный импульс (при 28 ат), сек.	5 Температура горения, °C
6 Кислород				
7 Диэтилентриамин ...	1,5	1,06	258	3065
8 Аммиак ...	1,3	0,88	255	2725
9 Этиловый спирт 75%-й	1,3	0,99	225	2845
10 » » 92,5-й	1,5	0,98	232	2950
11 Гидразин ...	0,75	1,06	267	—
12 Водород ...	8	0,43	360	—
13 JP-4 ...	2,3	0,98	247	3190
14 Октан ...	2,4	0,96	252	3200
15 Диметилгидразин ...	1,4	0,96	249	3120
16 Озон				
17 Озон + JP-4 ...	2,4	1,14	260	3525
18 Озон — 30% Кислород—70% } +JP-4	2,3	1,04	252	3290
19 Озон — 70% Кислород—30% } +JP-4	2,3	1,08	257	3415

1) Fuel; 2) weight ratio of oxidizer to combustible; 3) density at 27°; 4) specific impulse (at 28 atm), sec; 5) combustion temperature, °C; 6) oxygen; 7) diethylenetriamine; 8) ammonia; 9) 75% ethyl alcohol; 10) same, 92.5%; 11) hydrazine; 12) hydrogen; 13) JP-4; 14) octane; 15) dimethyl hydrazine; 16) ozone; 17) ozone + JP-4; 18) 30% ozone and 70% oxygen + JP-4; 19) 70% ozone and 30% oxygen + JP-4.

special "RP-1" rocket-engine kerosene. The physicochemical constants of this kerosene are more stable and it is more highly purified.

"RP-1" rocket kerosene has a heating value Q_n = 10,280 kcal/kg, a density of 0.8, a freezing point no higher than —40°, a flash point of —43.3° [sic], and a boiling range from 185 to 274°.

The use of "RP-1" kerosene in the US ballistic rockets "Thor" and "Atlas" and in the "Vanguard" space rocket has been reported [5].

The problem of using liquid hydrogen in rocket engineering is under intensive study in the USA.

Liquid hydrogen has been in production in the USA since 1957 at

two small plants, and by 1959 a plant had been placed in operation in Florida to produce several tons of hydrogen per day. The hydrogen is produced by partial oxidation of methane [C].

The liquid hydrogen is stored at the plants in special 106-m^3 tanks and in spherical reservoirs with capacities of $380\ \text{m}^3$. The evaporation losses in these containers come to 0.06 to 0.24% per day. The reservoirs are connected with the plants by pipelines to return the gaseous hydrogen, and the liquid-hydrogen pipelines are vacuum-insulated. Liquid pumps are used to transport the liquid hydrogen. Tractor-trailers carrying 26-m^3 tanks are used at the plant to haul the liquid hydrogen to its points of use.

A pipeline more than 1.6 km long was built from the plant to the test area to provide for engine testing. About $200\ \text{m}^3$ of liquid hydrogen was used in a single test.

Spilled hydrogen evaporates or burns; certain sources regard it as less of a fire hazard than gasoline. The possibility of using liquid hydrogen has been under study in the USA for more than 10 years. Thus, as long ago as 1952, tests of a fuel consisting of liquid hydrogen and oxygen in a static-test engine developing 1350 kg of thrust were reported.

Mixtures of hydrogen with oxygen and fluorine are characterized in Table 132a.

The largest engine developed for liquid hydrogen develops a thrust of 68 tons at the surface and has already been tested dozens of times. Engines developing 800 kg and 6800 kg of thrust are under development; these will be used for the last stages of the "Saturn" cosmic rocket vehicle in the USA.

Liquid hydrogen can be used as a working fluid for nuclear rocket engines.

TABLE 132a

Characterization of Fuel Mixtures Based on Hydrogen

1 Окислитель	2 Отношение окислитель: горючее	3 Плотность топлива	4 Температура горения, °C	5 Давление в камере, am	6 Удельный импульс (p/p₀=40).сек.
7 Кислород	3,4	0,26	2420	68	338
»	22,5	0,69	2580	58	244
»	3,5	0,26	—	33	366
»	2,9	0,23	2140	19,4	357
8 Озон	2,65	0,23	2420	19,4	373
9 Фтор	4,54	0,38	2500	68	398
»	29,80	0,91	4300	68	316
»	19,0	0,75	—	41	345
»	4,0	0,32	2700	41	381

1) Oxidizer; 2) oxidizer:combustible ratio; 3) density of fuel; 4) combustion temperature, °C; 5) chamber pressure, atm; 6) specific impulse $(p/p_0 = 40)$, sec; 7) oxygen; 8) ozone; 9) fluorine.

The physicochemical properties of liquid hydrogen are listed below and at the end of the book.

Molecular weight......................... 2.016
Boiling point, °C...................... −252.78
Melting point, °C...................... −259.1
Density of liquid H_2 at −252.7°........ −0.0695
Heat of evaporation at −252.7°......... 0.0695
Viscosity at −252.7°, centistokes...... $1.362 \cdot 10^{-4}$
Critical temperature, °C............... −239.9
Critical pressure, atm................. 12.8
Density at critical point.............. 0.031
Heating value at 25°................... 28,669
Heat content of liquid H_2 at −259°,
    kcal/mole·degree................. 3.31

Ozone was investigated in Germany (1942-1945) as an oxidizer for reaction-thrust engine fuels. Experiments indicated that gaseous and liquid ozone cannot be used for this purpose because of the high explosion hazard. Thus, gaseous mixtures of oxygen with ozone are capable of exothermic reaction (due to conversion of the ozone into oxygen) in the tanks and pipelines at ozone concentrations of even 10% by weight

and higher on local heating. However, the initiated reaction is capable
of stable self-propagation only at ozone concentrations of at least
17%. When such a mixture decomposes in a closed space, the pressure
rises to 2 atm. In gaseous mixtures containing 40-50% of ozone, a flame
appears on decomposition and the pressure rises to 6-10 atm. All this
renders difficult — if not excluding it altogether — the use of fuel
mixtures based on ozone, in spite of their high heat yields.
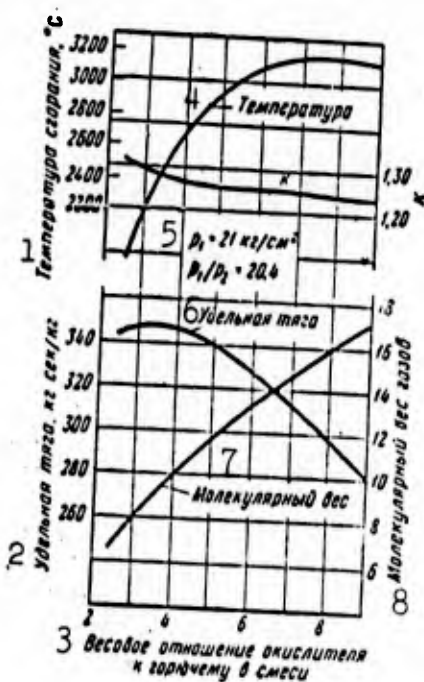
Fig. 187. Theoretical charac-
teristics of hydrogen-oxygen
fuel at various compositions.
1) Combustion temperature, $^\circ$C;
2) specific thrust, kg·sec/kg;
3) ratio of oxidizer to com-
bustible in mixture (by weight);
4) temperature; 5) $p_1 = 21$
kg/cm^2; 6) specific thrust; 7)
molecular weight; 8) molecular
weight of gases.

However [6], certain investigators regard it as quite feasible to
use ozone as an oxidizer in the form of a 20% solution in oxygen. Fac-
tory tests have been made with such a system.

Figures 187, 188, and 189 present theoretical characteristics of

- 506 -
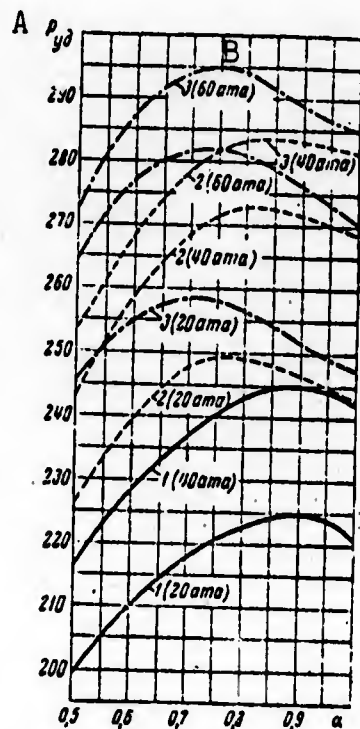
Fig. 188. Theoretical specific
impulse (P_{ud}) of a number of
fuels as a function of excess-
oxidizer ratio (α) at various
chamber pressures. 1) Kerosene-
nitric acid; 2) 93.5% ethyl
alcohol-liquid oxygen; 3) kero-
sene-liquid oxygen. A) P_{ud}; B)
(60 atm abs).

oxygen-based fuels with such combustibles as hydrogen, kerosene and
75% ethyl alcohol.

Figure 188 shows the theoretical specific impulse as a function
of excess-oxidizer ratio for various pressures, while Fig. 189 shows
the theoretical specific impulse of the A-4 engine's fuel (liquid oxy-
gen and 75% ethyl alcohol) for various altitudes.

At an altitude of 28-30 km, the specific impulse increases by 15-
17%, after which it undergoes no further change. The engine thrust in-
creases in accordance with the specific thrust. As will be seen from
Fig. 189, the theoretical and actual engine thrusts are quite similar
[2].

According to recent data, the specific thrusts of fuels at $p/p_0 =$

= 35 are as follows: kerosene-oxygen, 265; kerosene-fluorine, 275; oxygen-ammonia, 270; fluorine-ammonia, 305; hydrazine-oxygen, 280; hydrazine-fluorine, 320; and hydrogen-fluorine, 375 sec.

Table 133 lists the composition of the combustion products and the basic parameters of the process as functions of the fuel-mixture composition for a liquid-oxygen-and-gasoline fuel.

TABLE 133

Characteristics of Combustion Process of Fuel Consisting of Liquid Oxygen and Gasoline [2]

1) Состав продуктов сгорания в камере двигателя при температуре горения, молярные доли	2) Состав топлива, %						
	O_2 — 50, бензин —50	O_2 — 66, бензин —34	O_2 — 69,2, бензин —30,8	O_2 —72,4, бензин —21,6*	O_2 —73,6, бензин —26,4	O_2 —75, бензин —25	O_2—77,3, бензин —22,7**
CO	0,455	0,411	0,37	0,322	0,280	0,243	0,198
CO_2	0,023	0,079	0,109	0,137	0,160	0,180	0,202
H_2	0,382	0,215	0,152	0,105	0,079	0,057	0,038
H_2O	0,125	0,278	0,326	0,330	0,330	0,325	0,305
H	0,000	0,012	0,026	0,028	0,027	0,025	0,021
OH	0,000	0,009	0,028	0,061	0,085	0,104	0,124
O_2	0,000	0,000	0,003	0,008	0,019	0,028	0,085
O	0,000	0,000	0,002	0,006	0,010	0,016	0,026
4) Температура, °C	1480	2590	2850	3020	3090	3110	3130
5) Удельный импульс, сек.	200	236	240	242	241	238	234

*α — 0.92.
**α — 1.0.

1) Composition of products of combustion in engine chamber at various [see column heads] combustion temperatures and molar proportions; 2) fuel composition, %; 3) gasoline; 4) temperature, °C; 5) specific impulse, sec.

Table 134 shows the influence of pressure on the combustion characteristics of the fuel.

With increasing combustion-chamber pressure, the specific thrust increases and the combustion temperature rises slightly.

Alcohols [3, 5, 6, 7] were used as combustibles in the first engines. 75% ethyl alcohol and liquid oxygen were used as a fuel in the German long-range A-4 rocket. Alcohols are still of some importance at
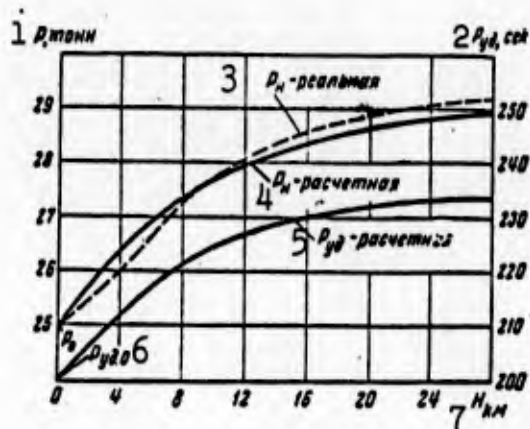
Fig. 189. Theoretical specific impulse of A-4 engine burning liquid oxygen and 75% ethyl alcohol and theoretical and actual engine thrusts as functions of altitude. P_{ud} is the theoretical specific impulse and P_n is the theoretical (solid line) or actual (broken line) engine thrust. 1) P, tons; 2) P_{ud}, sec; 3) P_n (real); 4) P_n (theoretical); 5) P_{ud} (theoretical); 6) $P_{ud.0}$; 7) H, km.

the present time as rocket combustibles [8].

Let us consider the properties of the homologous series of aliphatic saturated alcohols from the standpoint of their usefulness as rocket-engine combustibles (Table 135).

TABLE 134

Influence of Pressure on Combustion Characteristics of Fuel Consisting of 75% Ethyl Alcohol and Oxygen [2]

1 Характеристика	2 Давление в камере, ат		
	10	20	50
3 Температура, °C	2574	2585	2613
4 Удельный импульс, сек. . . .	210	233	256

1) Characteristic; 2) chamber pressure, atm; 3) temperature, °C; 4) specific impulse, sec.

Alcohols from methyl to propyl have a slightly lower efficiency

TABLE 135

Comparative Characterization of Fuel Mixtures
Based on Alcohols and Cyclohexane [2]

1 Горючее	2 Формула	3 Т. пл., °C	4 Тепло-творная способ-ность, ккал/кг	5 Состав топлива, %		8 Удельное газообра-зование, л/кг	9 Удельная теплопро-изводи-тельность, ккал/кг	10 Ско-рость истече-ния, м/сек *
				6 спирт	7 кисло-род			
11 Метиловый спирт	CH_3OH	— 94,9	5330	40	60	839	1870	2380
12 Этиловый »	C_2H_5OH	—	7180	32,4	57,6	789	2020	2410
13 Пропиловый »	C_3H_7OH	—127	8050	29,4	70,6	768	2100	2550
14 Бутиловый »	C_4H_9OH	— 89,8	8600	27,3	72,7	763	2200	2610
15 Гексиловый »	$C_6H_{13}OH$	— 51,6	—	22,7	77,4	748	2270	2660
16 Циклогексан	C_6H_{12}	—	—	—	—	747	2280	2660

*In a fuel mixture with oxygen at 25 atm.

1) Combustible; 2) formula; 3) melting point, °C;
4) heating value, kcal/kg; 5) fuel composition, %;
6) alcohol; 7) oxygen; 8) specific gas production,
liters/kg; 9) specific heating yield, kcal/kg; 10)
outflow speed, m/sec*; 11) methyl alcohol; 12)
ethyl alcohol; 13) propyl alcohol; 14) butyl al-
cohol; 15) hexyl alcohol; 16) cyclohexane.

in fuel mixtures than hydrocarbons. The combustion-product exit speed

for a fuel based on methyl alcohol is 2380 m/sec, and that for a fuel

based on ethyl alcohol is 2410 m/sec, i.e., values lower than that for

a fuel based on oxygen and cyclohexane, for which we have 2660 m/sec.

At the same time, the combustion temperatures of ethyl and propyl al-

cohols are lower than those of the hydrocarbons; this is the great ad-

vantage of alcohol-based fuels.

As regards their melting points, alcohols from methyl to hexyl

(melting point —51.6°) satisfy rocket-fuel requirements. It is inter-

esting to direct our attention to the fact that the specific heating

values of the lower alcohols are much lower than those of the hydrocar-

bons: by almost 50% for methyl alcohol and 30% for ethyl alcohol. At

the same time, the heating yield drops by only 9-18% in fuel mixtures

of alcohols with oxygen. As a result, the combustion-product outflow

speed and specific thrust for fuels based on the lower alcohols are

only 9-10% lower than those for fuels based on hydrocarbons.

In addition to the lower combustion temperatures as compared with hydrocarbons, alcohols have still other advantages related to their physical properties (Table 136). One of these properties of, for example, the lower alcohols, is their excellent solubility in water, which makes it possible to use them in aqueous solutions. This results in a drop in the combustion temperature of the fuel in the engine. Aqueous solutions of alcohols also possess good coolant properties.

Analysis of the data in Table 136 indicates that the lower alcohols have higher heat capacities than do petroleum products. Alcohols may be injected into the fuel mixture in large quantities, and this makes possible superior cooling of the engine-chamber walls as they are washed by the combustible. Moreover, the lower alcohols have latent heats of evaporation that are 3 to 4 times higher than those of petroleum products. This also promotes better cooling of the inner chamber liners of the engine on evaporation of the alcohol, particularly when it is mixed with water.

TABLE 136

Physicochemical Properties of Certain Alcohols, Water and Kerosene

1 Вещество	2 Растворимость в воде, %	3 Т. кип., °C	4 Теплоемкость (при 20—25°), ккал/кг·град	5 Скрытая теплота испарения, ккал/кг	6 Вязкость при 20°, ccm
CH$_3$OH	7 Неограниченная	64,6	0,600	263	0,548
C$_2$H$_5$OH	•	78,3	0,58	214,5	1,76
C$_3$H$_7$OH	•	97,8	0,59	159,4	2,195
C$_4$H$_9$OH	5,6	117,7	0,5	143,0	—
C$_5$H$_{11}$OH	2	137,9	0,5	120,19	4,5
8 Вода	—	100	1,00	536	1,0
9 Керосин	—	150—300	0,45	51	3,0

1) Substance; 2) solubility in water, %; 3) boiling point, °C; 4) heat capacity (at 20-25°), kcal/kg· ·deg; 5) latent heat of evaporation, kcal/kg; 6) viscosity at 20°, centistokes; 7) unlimited; 8) water; 9) kerosene.

TABLE 137

Characterization of Fuels Based on Liquid
Oxygen and Ethyl Alcohol

1 Характеристика горючего	2 Состав топлива, %		5 Теплопроизводительность, л/кг	6 Удельное газообразование, л/кг	7 Характеристика охлаждающих свойств *
	3 кислород	4 спирт			
8 Спирт:					
100%	67,60	32,4	2020	870	1,9
95%	66,4	33,6	1960	797	—
90%	65,11	34,89	1935	805	2,2
85%	63,9	36,1	1880	814	—
80%	62,53	37,47	1820	823	2,4
75%	61,0	39,0	1770	834	—
70%	59,4	40,60	1705	845	2,8
60%	55,6	44,4	1560	870	—
9 Керосин	75,80	24,20	2280	—	1,0

*Relative heat required to heat combustible
to boiling point with total evaporation.

1) Combustible; 2) composition of fuel, %;
3) oxygen; 4) alcohol; 5) heating yield,
liters/kg [sic]; 6) specific gas production,
liters/kg; 7) characteristic of coolant prop-
erties*; 8) alcohol; 9) kerosene.

A characterization of fuels based on oxygen and ethyl alcohol at
various concentrations appears in Table 137.

Cyanogen and other unsaturated compounds containing triple bonds
and having negative heats of formation are under consideration as pos-
sible combustible components for rocket fuels.

This group includes acetonitrile, dicyanogen, and acetylene di-
nitrile. Their combustion in oxygen proceeds in accordance with the
following reaction:

$$N \equiv C - C \equiv N + 2O_2 \rightarrow 2CO_2 + N_2.$$
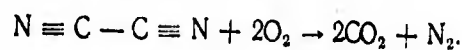
The characteristics of these fuels are listed in Table 138.

The combustion of cyanogen derivatives is attended by high tem-
perature. Thus, the temperature reaches $4640^{\circ}K$ in the case of dicyano-
gen and $5300^{\circ}K$ in the case of acetylene dinitrile.

A considerably higher specific impulse can be obtained with cy-

TABLE 138

Characteristics of Fuel Mixtures
Based on Nitriles

1 Топливо	2 Теплота образования горючего, ккал/моль	3 Теплопроизводительность, ккал/кг	4 Удельный импульс $(p/p_0 = 50)$, сек.
$CH_3CN + O_2$	— 10,9	2200	303
$N{\equiv}C{-}C{\equiv}C{-}C{\equiv}N + O_2$	--130,0	2440.	310
5 Циклогексан $+ O_2$	$+$ 37,0	2970	300

1) Fuel; 2) heat of formation of combustible, kcal/mole; 3) heating value,
kcal/kg; 4) specific impulse $(p/p_0 =$
$= 50)$, sec; 5) cyclohexane $+ O_2$.

anogen derivatives than with kerosene.

Apart from oxygen and oxidizers based on it, the use of fluorine
and its compounds as oxidizers is conceivable [9]. Fluorination of organic compounds is accompanied by liberation of a large quantity of
heat [10], e.g., for heptane:

$$C_7H_{16} + 16F_2 \rightarrow C_7F_{16} + 16HF + 1660 \text{ kcal},$$
$$C_7H_{16} + 22F_2 \rightarrow 7CF_4 + 16HF + 2211 \text{ kcal}.$$
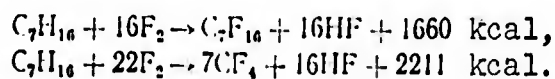
In the case of complete combustion, the heat effect of the reaction per kg of fuel mixture comes to 2650 kcal/kg.

The final products of combustion of hydrocarbons in fluorine are
hydrogen fluoride and carbon tetrafluoride.

Fluorine possesses exceptionally high chemical activity and can
cause ignition with a number of organic materials in the liquid state
[11]. Fluorine is highly toxic, causing inflammation of the respiratory
tract. An isolating gas mask is required for protection from it, since
the activated carbon of a filtering gas mask oxidizes readily after absorption of a sufficient quantity of fluorine.

The use of fluorine as a rocket oxidizer is possible only when it
is in its liquid form, i.e., at its boiling point of -187°. However,

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such use of fluorine would require development of methods for trapping and condensing fluorine vapor and protecting the servicing personnel from its effects.

Copper, nickel and even steel are used as structural materials for the storage of fluorine. Thus, for example, fluorine was stored in Germany in steel bottles under a pressure of 30 atm [11].

In recent years, fluorine has been under intensive study as an oxidizer for rocket engineering, and these studies have been going on for more than 10 years in the USA.

Thus, it was reported in 1958 [12-14] that the firm Bell in the USA was experimenting with fluorine in combination with hydrazine and dimethyl hydrazine in a rocket engine developing a thrust of 16 tons.

In 1959, plans for static engines to burn fluorine and develop thrusts of 5.5 and 36 tons were under consideration. The projected research program required 1000 tons of liquid fluorine per year.

One of the major problems in using fluorine in rocket engines was the transportation and storage of liquid fluorine. This problem is now regarded as solved. Thus, fluorine is stored and transported in special 2.3- and 25-ton tanks with a daily loss no greater than 0.75% of the load, and can be stored from 15 to 25 days. The basic problem here is preventing escape of fluorine into the atmosphere, since in view of its high toxicity, the maximum admissible fluorine concentration in the air may not exceed 0.0001%.

The combustion products of fluorine-containing fuels are also toxic, but the use of these fuels in the second and subsequent stages of the rocket will not represent difficulty from the viewpoint of toxicity. However, setting up static tests of engines operating on fluorine oxidants, taking contamination of the atmosphere into account, is an extremely complex problem.

The theoretical characteristics of fuels based on fluorine and its compounds (according to North American) for a pressure drop $p/p_0 = 28$ are listed in Table 139, while Table 140 shows a series of specific-impulse values for fluorine oxidants with various combustibles.

According to M.I. Shevelyuk [7], the theoretical characteristics of fuels based on fluorine have the following values for $p/p_0 = 40$:

	Specific impulse, sec	Combustion temperature, $^{\circ}C$
Fluorine-hydrazine.................	345	4217
Fluorine-ammonia....................	340	4252
Fluorine-ammonia (50%), hydrazine (50%)............................	342	4122
Fluorine oxide-kerosene.............	320	4257
Fluorine oxide-diethylamine.........	330	4137
Chlorine trifluoride-hydrazine......	285	3587
Oxygen-kerosene.....................	282	3337

According to the same author, the heating value of a fluorine-kerosene fuel is 2680 kcal/kg, and that of the oxygen-kerosene fuel is 2280 kcal/kg.

The specific impulse of fuels based on fluorine is considerably higher than those of oxygen-based fuels, and the combustion temperature is also higher — by almost 1000°.

We compare the specific-impulse values for fuels based on fluorine and oxygen according to other sources [8]:

	Specific impulse with pressure drop p/p_0, sec		
	28 atm	35 atm	40 atm
Fluorine-kerosene......	275	275	295
Oxygen-kerosene........	267	265	282
Fluorine-hydrazine.....	280	320	345
Oxygen-hydrazine.......	267	280	298

Apparently of interest is the use of combustibles such as boron,

beryllium and lithium in fluorine-based fuels, as will be evident from consideration of the following fuel mixtures:

	Heating yield, kcal/kg	Specific impulse $(p/p_0 = 50)$, sec
Fluorine-pentaborane (B_5H_9)........	3700	400
Fluorine-decaborane $(B_{10}H_{14})$.......	3740	395
Fluorine-boron......................	3940	330
Fluorine-silicon....................	3570	284
Fluorine-lithium....................	3300	405
Fluorine-hydrazine.................	2450	355

Boranes and alkyl-substituted boranes in combination with fluorine are definitely of interest.

Apart from fluorine, a certain amount of interest attaches to a series of oxidizers based on it (Tables 139 and 140).

In the USA, chlorine trifluoride is regarded as a potential oxidant for rocket fuels that would be comparable to nitric acid. Let us consider the characteristics of a number of fuels based on ClF_3 and HNO_3.

1 Окислитель	2 Горючее	3 Плотность топлива, g/cm^3	4 Удельный импульс $(p/p_0 = 42)$, сек.
ClF_3	$N_2H_4 + H_2N_2(CH_3)_2$	1,45	260
ClF_3	$H_2N_2(CH_3)_2 + NH (C_2H_4NH_2)_2$	1,43	251
ClF_3	5 Керосин RP-1	1,41	245
HNO_3, N_2O_4	» RP-1	1,30	245

1) Oxidizer; 2) combustible; 3) fuel density, g/cm^3;
4) specific impulse $(p/p_0 = 42)$, sec; 5) kerosene RP-1.

As compared with liquid-oxygen-based fuels, fluorine-based fuel has a considerably greater density and a somewhat larger specific thrust; this should ensure long flight ranges for rockets.

Fluorine oxide is also distinguished by this same advantage over liquid oxygen.

TABLE 139

Characteristics of a Number of Liquid-Rocket Fuels Based on Fluorine and its Compounds

1 Топливо	2 Весовое отношение окислитель: горючее	3 Плотность при 27°	4 Удельный импульс при 28 ат, сек.	5 Температура горения, °C
6 *Фтор*				
7 JP-4	2,9	1,19	275	3980
8 Аммиак	3	1,16	300	4020
9 Гидразин	2	1,3	280	4280
10 Водород	9,4	0,46	330	4480
11 *Дифторид кислорода*				
12 н. Октан	3,8	1,22	—	4060
13 Гидразин	1,1	1,23	257	3520
14 *Трифторид хлора*				
15 Аммиак	3	1,26	238	2750
16 Гидразин	2,5	1,16	247	3875
17 *Пентафторид брома*				
18 Аммиак	6	1,8	245	3680

1) Fuel; 2) oxidizer:combustible weight ratio; 3) density at 27°; 4) specific impulse at 28 atm, sec; 5) combustion temperature, $^\circ C$; 6) fluorine; 7) JP-4; 8) ammonia; 9) hydrazine; 10) hydrogen; 11) oxygen difluoride; 12) normal octane; 13) hydrazine; 14) chlorine trifluoride; 15) ammonia; 16) hydrazine; 17) bromine pentafluoride; 18) ammonia.

Chlorine trifluoride has no advantages as an oxidizer for long-range rockets with conventional combustibles.

Figure 190 shows the variation of specific thrust as a function of the weight fraction of fluorine in the fuel for a hydrazine-fluorine fuel.

Fluorine has advantages as an oxidizer for a number of metals and nonmetals such as magnesium, silicon and boron. With the last two, it forms gaseous combustion products (SiF_4 and BF_3) [11-13].

Apart from the energy indicators of the fuels, the combustion

TABLE 140

Specific Impulse of a Series of Fuels
Based on Fluorine and its Compounds

1 Топливо	2 Весовое отношение, окислитель : горючее	3 Удельный импульс $(p/p_0 = 42)$, сек.
4 Фтор — керосин	—	282
5 Фтор — гидразин	2,08	318
6 Фтор — водород	4,49	·381
7 Трифторид хлора — несимметричный диметилгидразин	2,55	274
8 Перфторид хлора — гидразин	1,1	274
9 Трифторид хлора — гидразин . . .	2,1	268
10 Пентафторид брома — гидразин	2,19	225
11 Трифторид азота — гидразин	2,64	276
12 Дифторид кислорода — несимметричный диметилгидразин	1,8	317
13 Кислород — керосин	2,4	272

1) Fuel; 2) oxidant:combustible
weight proportions; 3) specific im-
pulse $(p/p_0 = 42)$, sec; 4) fluorine-
kerosene; 5) fluorine-hydrazine; 6)
fluorine-hydrogen; 7) chlorine tri-
fluoride-unsymmetric dimethylhydra-
zine; 8) chlorine perfluoride-hydra-
zine; 9) chlorine trifluoride-hydra-
zine; 10) bromine pentafluoride-
hydrazine; 11) nitrogen trifluoride-
hydrazine; 12) oxygen difluoride-
unsymmetric dimethylhydrazine; 13)
oxygen-kerosene.

rates of fuels based on oxygen and fluorine in the liquid-fuel rocket
engine are of great significance.

Development of lightweight combustion chambers for high-powered
rocket engines involves solution of the problem of attaining high heat-
evolution rates in the combustion zone. Until recently, it was be-
lieved that physical processes (evaporation of drops, mixing, etc.)
represented limiting factors.

Recently, serious attention has been attracted to the question as
to whether the rate of chemical reaction in a gaseous medium cannot,
under certain circumstances, become the factor determining the rate of
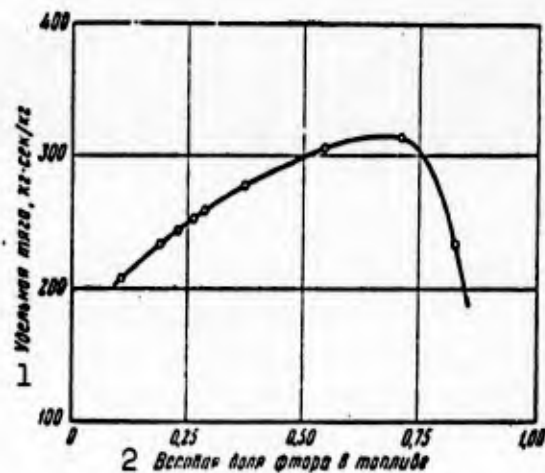
Fig. 190. Variation of theoretical
specific thrust (specific impulse)
of hydrazine-fluorine fuel as a func-
tion of weight fraction of fluorine
in fuel with $p/p_0 = 21$. 1) Specific
thrust, kg·sec/kg; 2) weight frac-
tion of fluorine in fuel.

the process [15]. In this connection, the rate of rocket-fuel heat evo-
lution was computed for various conditions from the rate of the chem-
ical reaction, proceeding from the equation of N.N. Semenov, in which
the normal combustion rate is linked to the rate of the reaction:

$$ U = \frac{1}{\rho_0 L_0} \sqrt{2\lambda_f Q \int_0^{T_f} \omega \, dT}, $$

where ρ_0 is the density of the fuel mixture, L_0 is the heat of combus-
tion (cal/g), λ_f is the thermal conductivity, Q is the heating value
($cal/mole$), T_f is the adiabatic combustion temperature, ω is the rate
of the chemical reaction in the temperature range from T_0 to T_f, and
U_f is the rate of laminar combustion.

This equation is modified:

$$ U_f = \sqrt{\frac{2\lambda_f}{C_p} \cdot \frac{RT_0}{p\Delta H_v} \cdot \bar{q} \cdot \left(\frac{1}{F}\right)}, $$

where λ_f is the thermal conductivity, C_p is the heat capacity, p is the
pressure, ΔH_v is the heat of combustion per unit volume ($kcal/cm^3$), $\bar{q}$

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TABLE 141

Volume Rates of Heat Evolution for Various
Rocket Fuels

1 Топливо	2 Давление, ат	3 Адиабатическая температура горения, °C	4 Энергия активации, кал/моль	5 Нормальная скорость горения, см/сек	6 Максимальная скорость тепловыделения, ккал/м³·час
$C_8H_{18} + O_2$	1	3056	40 000	400	$4 \cdot 10^{12}$
$C_8H_{18} + O_2$	15	3422	40 000	688	$2,4 \cdot 10^{15}$
$NH_3 + O_2$	1	2782	49 500	110	$1,3 \cdot 10^{11}$
$NH_3 + O_2$	15	3041	49 500	110	$2,7 \cdot 10^{13}$
$H_2 + O_2$	1	3018	18 000	1010	$4,1 \cdot 10^{12}$
$H_2 + O_2$	15	3384	18 000	3417	$1 \cdot 10^{16}$
$H_2 + F_2$	1	3962	5 000	10 000	$6,4 \cdot 10^{14}$
$H_2 + F_2$	15	4546	5 000	33 800	$1,4 \cdot 10^{18}$
$H_2 + F_2$	1	3962	10 000	—	$6,8 \cdot 10^{14}$

1) Fuel; 2) pressure, atm; 3) adiabatic com-
bustion temperature, °C; 4) activation energy,
cal/mole; 5) normal rate of combustion,
cm/sec; 6) maximum rate of heat evolution,
kcal/m^3·hr.

TABLE 142

Comparison of Theoretical Rates of
Heat Evolution with Experimental
Rates in Rocket Engine

1 Топливо	2 Давление, ат	3 Объемная скорость выделения тепла, ккал/м³·час	
		4 экспериментальная в ЖРД	5 расчетная
6 н. Гептан — жидкий O_2	18,4	$6,31 \cdot 10^9$	$3,56 \cdot 10^{15}$
7 Жидкий H_2 — жидкий O_2	10,9	$3,47 \cdot 10^9$	$1,78 \cdot 10^{13}$
8 Газообразный H_2—жидкий O_2	20,4	$7,47 \cdot 10^9$	$1,78 \cdot 10^{16}$
9 Газообразный H_2—жидкий O_2	25,2	$7,56 \cdot 10^9$	$6,23 \cdot 10^{18}$

1) Fuel; 2) pressure, atm; 3) volume
rate of heat evolution, kcal/m^3·hr;
4) experimental, in liquid-fuel
rocket engine; 5) theoretical; 6)
normal heptane-liquid O_2; 7) liquid
H_2-liquid O_2; 8) gaseous H_2-liquid
O_2; 9) gaseous H_2-liquid O_2.

is the average volume rate of heat evolution ($cal/cm^3 \cdot sec \cdot atm$), and R is a factor equal to $2.4213 \cdot 10^{-2} \; cal/cm^3 \cdot atm$.

By transforming this last equation, we obtain the following expression for calculating rate of heat evolution:

$$q_{max} = \frac{F}{F(n+1)} \cdot \frac{E}{RT_l} \cdot \frac{T_l - T_0}{T_l} \cdot \frac{n}{C} \cdot \frac{C_p}{2\lambda_l} \cdot \frac{T}{RT} \cdot U]\Delta H_{v.}$$

where $\underline{n}$ is the order of the reaction and E is the activation energy.

The data shown in Table 141 were calculated according to this equation.

The calculations were carried out for stoichiometric composition of the mixture and two pressures, 1 and 15 atm.

The rate of heat evolution is highest for hydrogen with fluorine.

Table 142 lists volume heat-evolution rates observed in rocket engines, and, for comparison, the theoretical values.

The rate of heat evolution was determined in experimental engines from the rate of fuel infeed and the completeness of its combustion.

It is evident from the experimental and theoretical data listed that only a minor fraction of the possible volume rate of heat evolution is realized in contemporary rocket engines.

The theoretical volume rate of heat evolution in liquid-fuel rocket engines may be increased by several orders and the size of the combustion chamber reduced accordingly.

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Manu-script Page No.	[Footnote]
501	Dimethylhydrazine was used with oxygen in the first-stage engine of the rocket used to launch an artificial Earth satellite in the USA on 31 January 1958 [4].

Manu-script Page No.	[List of Transliterated Symbols]
503	н = n = nizshiy = lower-limit
507	уд = ud = udel'nyy = specific

Chapter 8

MONOPROPELLANTS FOR LIQUID REACTION ENGINES

Propellants for liquid reaction engines are classified on the basis of the method of propellant accomodation and supply as: a) bipropellants, consisting of an oxidizer and a combustible supplied separately to the combustion chamber (from two tanks), and b) monopropellants, which include oxidizer and combustible elements, and which are supplied from a single tank.

Despite the advantage offered by monopropellants in comparison with bipropellants, they have not as yet received widespread application as power sources for rocket motors. The reason for this is that the presently known monopropellants having heating yields of from 1000-1500 kcal/kg and specific impulses of 200-245 sec, are liable to explode under the conditions governing their use in rocket motors.

On the other hand, the low-energy-yield explosion-proof monopropellants presently employed are used solely in turbopump units of ZhRD, where the energy characteristics are not the chief consideration.

A monopropellant offers the following advantages in comparison with bipropellants.

1. A motor installation for a monopropellant is simplified, since one propellant tank and half of the piping may be eliminated.

2. In a monopropellant motor installation, there is no need for a special device to maintain the propellant-component ratio constant; this permits a decrease in the emergency reserves of propellant.

3. There is a substantial simplification in the motor-head struc-

ture in connection with the fact that a monopropellant does not require good component mixing upon injection into the combustion chamber. In many cases, unstable combustion of bipropellants in a rocket motor is related to unsatisfactory mixing of the combustible and oxidizer, which is eliminated in monopropellant motors.

4. It is possible to use the full flow of a monopropellant for regenerative motor cooling; this simplifies the cooling problem, anu permits a considerable decrease in fuel losses due to internal cooling of the combustion chamber and nozzle.

5. Rockets using monopropellants will be more reliable, owing to the decrease in the number of propellant components and the simplification of the motor installation.

Calculations indicate that for medium-range rockets, a monopropellant having a specific impulse of 225 sec is equivalent to a bipropellant having a specific impulse of 250 sec, a fact explained by the simplicity of the monopropellant motor arrangement.

Monopropellants may take the form of individual compounds such as nitromethane, methylnitrate, as well as solutions of nitro and chlorine derivatives of hydrocarbons in nitric acid. These systems may have heating yields of 750-1500 kcal/kg. All of these substances have explosive properties, present in various degrees.

For this reason, monopropellants may be dangerous to handle, and they are not as widely employed as are separately supplied propellants.

Systems that liberate large quantities of heat and gases upon combustion in a ZhRD chamber may be considered as monopropellants. They include the following propellants.

1. Propellants based upon solutions of organic substances in nitric acid and oxides of nitrogen. The organic substances in solution should be stable with respect to nitric acid.

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2. Propellants based upon nitro compounds (nitromethane) and nitro ethers (ethylnitrate, propylnitrate).

3. Propellants based upon solutions of organic substances in tetranitromethane.

4. Propellants based upon hydrogen peroxide and solutions of organic substances in hydrogen peroxide.

5. Propellants based upon many other compounds that can break down with the evolution of heat.

Only those monopropellants may be utilized in practice that are sufficiently safe to handle and use. It is an extremely complicated matter to select such propellants.

Under certain conditions, monopropellants behave as fuels, and under other conditions as explosives; in this connection, it is first desirable to examine the explosive properties of these systems, and then to turn to individual types of monopropellants.

1. Characteristics of Monopropellant Explosive Properties

a) Conditions for appearance of explosive reaction

By explosive properties, we mean conditions for the appearance of an explosive reaction: sensitivity to heating, shock, friction, the mechanical effect of explosion.

Depending upon the reaction rate, systems containing combustible and oxidizer elements (powders, explosives, monopropellants) are divided into two basic reaction types: a) normal combustion, b) explosion and detonation [1, 2].

At atmospheric pressure, the combustion process in liquid and solid monopropellants takes place at a rate measured in the millimeters or (at a pressure of 40-75 atm) centimeters per second. An increase in the mass of the burning material may occur as a result of an increase in the combustion surface, by a change in the grain size of a powder,

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and through an increase in the degree of dispersion of a liquid fuel.

An explosion is characterized by the fact that the explosive chemical reaction propagates at a rate of the order of hundreds and thousands of meters per second. An explosive reaction rate is characterized as a nonsteady-state quantity, varying in many cases as a function of the conditions under which the explosion has been initiated.

Detonation is characterized as a steady-state propagation rate for the explosive reaction over the mass of the substance — of the order of 3000-8000 m/sec. The maximum speed of a detonation is a constant characteristic of each explosive. Decomposition in the form of detonation and explosion can evidently occur under appropriate conditions for any system capable of supporting an exothermic reaction.

TABLE 143

Explosive Properties and Heating Value of Certain Systems [1, 2]

1 Соединение	2 Формула	3 Теплопроизводительность, ккал/кг	4 Способность к горению в трубке	5 Способность к детонации от стандартного детонатора	6 Детонация от 10 г-ой навески ВВ
7 Нитрометан	CH_3NO_2	1030	Горит	Не взрывает	Взрывает
8 Тротил	$CH_3C_6H_2(NO_2)_3$	1010	*	Взрывает	—
9 Азотнокислый аммоний	NH_4NO_3	344	Не горит	Не взрывает	Не взрывает
10 Смесь азотнокислого аммония с сульфатом аммония	$NH_4NO_3 + (NH_4)_2SO_4$	250	» »	» »	» »
11 Тетранитрометан	$C(NO_2)_4$	500	» »	» »	» »
12 Азид свинца	PbN_6	367	Взрывает		

*In open charge.

1) Compound; 2) formula; 3) heating value, kcal/kg; 4) ability to burn in tube; 5) ability to be detonated by standard detonator; 6) detonation by 10-g grain of explosive; 7) nitromethane; 8) trotyl; 9) ammonium nitrate; 10) mixture of ammonium nitrate with ammonium sulfate; 11) tetranitromethane; 12) lead azide; 13) burns; 14) does not burn; 15) does not explode; 16) explodes.

A necessary condition for the explosive reaction of a system is a positive heat yield from the reaction at an adequate rate, accompanied

by the formation of gaseous products. Since the system goes from the solid or liquid state to the gaseous state almost instantaneously, while the gaseous products occupy a volume roughly 1000 times greater than that taken up by the initial substance, and is at high temperature, an instantaneous pressure jump is set up at the point of explosion, amounting to tens and even hundreds of thousands of atmospheres.

A well-known characteristic of liability to explosive decomposition is the heating value of the explosive system. Thus, tetranitromethane, whose heat of decomposition is positive and roughly 500 kcal/kg, is a safe material in practice, under normal conditions. Selfpropagation of an explosive reaction is hindered by a low heat yield.

In the general case, however, the heating value is not a criterion of explosiveness. Thus, the detonator lead azide PbN_6 explodes very easily, although its heating yield is 367 kcal/kg.

In this connection, it is interesting to examine certain systems: their ability to participate in an exothermal reaction, and their liability to detonation (Table 143).

An explosive reaction is a chemical reaction whose initiation is opposed by a certain energy barrier. The magnitude of the energy barrier is determined by the activation energy.

The liability of a system to explosive reaction is determined by a complex of phenomena: the activation energy, the heat yield of the reaction, and the physical conditions under which the substance is found.

Lead azide has a low activation energy for initiation of an explosion. Thus, it may easily be detonated, even by kindling.

Liquid explosives based upon nitric acid have a large heating yield. Owing to their high activation energy, however, they are relatively insensitive to explosion.

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The heat of decomposition of the oxidizers in explosive mixtures plays a substantial role. Where the heat of decomposition of the oxidizer is positive, explosive mixtures are very explosion-sensitive.

Physical factors have a considerable effect upon the possibility of explosion propagation.

For many substances, steady-state propagation of a detonation is possible only in the case in which the charge diameter is relatively large. Thus, for trinitrotoluene, the charge diameter should exceed several millimeters.

For low-sensitivity liquid explosives, detonation will not propagate in sufficiently thin tubes. As Yu.B. Khariton [3] has shown, this is connected with the fact that upon passage of the blast wave through the mass of the substance, there is in addition to the chemical reaction a dispersion of the initial substance along the front of the blast wave, i.e., in the region where the explosive is converted to explosion products. The explosive reaction is retarded by the dispersion of the initial material.

The dispersion time is roughly proportional to the charge diameter. If the time required to complete the explosive reaction is less than the dispersion time, the detonation will propagate through the charge of substance.

Any factor increasing the dispersion time such as, for example, an increase in charge diameter, or the placing of the charge into a massive jacket, should improve detonation propagation; this is actually observed to be the case.

It is very important in practice to allow for the possibility of detonation propagation. Thus, for example, in order to avoid the propagation of a detonation of a monopropellant from the motor to the tanks, the piping must be chosen with a diameter for which propagation of a

detonation is impossible. Here it is necessary to allow for the possibility of detonation propagation through the air.

Certain systems, capable of participating in an exothermal reaction, will not explode in open charges, but do become liable to detonation in a strong jacket.

Although in theory, any system capable of reacting exothermally and for which the thermal and mechanical effect of the explosion products accelerate the chemical reaction is liable to explosive reaction; there may exist systems, however, for which the creation of charges with a diameter providing a stable detonation is impractical, since this diameter would be too large.

On the other hand, many substances and mixtures which are not explosive in practice under normal conditions may explode if the charge dimensions are sufficiently large, and if the explosion is correctly initiated.

Yu.B. Khariton [3] assumes the following mechanism for detonation propagation.

1) At first, the substance is compressed as a result of a shock wave. The compression causes heating, followed by a chemical reaction. This is the way in which a detonation propagates in gases.

2) The explosive-reaction process may occur as a result of combustion of separate particles of the substance — their ignition. The majority of solid explosive substances are quite brittle, and it is thus highly probable that in the detonation process, the material will break down into fine particles. In accordance with this mechanism, liquid explosives disperse into fine drops. The more the substance breaks down, the greater the reaction rate, since the rate of particle combustion is roughly proportional to size. Assuming that at very high pressures, the combustion rate in the explosion wavefront will

be very high, a high explosion reaction rate will be created.

3) The reaction along the blast-wave front may be associated with the reaction of two or several substances occurring in the form of particles of some degree of dispersion, or in the form of a mixture of solid particles and liquid. In this case, the explosive mixture is heterogeneous, and the reaction will not take place throughout the entire volume of the substance lying along the detonation-wave front, but only at the interface between components, or in regions where the components have already formed a molecular mixture.

For large particle dimensions, an explosive reaction may in general turn out to be impossible, since the required mixing will not occur.

b) Determination of susceptibility to heating, shock, and friction

Susceptibility to heating is characterized by the flash point, i.e., the lowest temperature to which the substance must be heated in order for it to ignite. Various methods may be used to determine the flash point [1, 2, 4].

The substance is placed into a test tube previously heated to a specific temperature. The determination is made of the lowest temperature at which instantaneous ignition occurs. If a flash does not occur, the temperature is raised, and the experiment repeated with a new portion of substance. If a flash does occur, the temperature is somewhat decreased, and the experiment repeated, thus, the minimum flash point is found to within 5°. The "instantaneous" flash is an arbitrary concept, and characterizes a flash occurring with no visually apparent ignition lag.

In order to determine the flash point of a liquid monopropellant, the substance is placed into a capillary tube open at both ends, having a diameter of 1-2 mm; the capillary tube is emptied into the heated

test tube. A tap on the bottom of the test tube causes the substance to flow out from the capillary to the heated bottom of the test tube; ignition results. In flash-point determination, safety precautions must be taken: a panel of thick glass or transparent plastic should be placed before the bath, and the eyes of the experimenter should be protected by goggles.

The flash point depends upon the conditions under which the determination is made, and with existing methods, it may be considered to be an approximate quantity characterizing the sensitivity of a propellant to thermal effects.

Shock susceptibility characterizes the danger of monopropellant explosion in handling.

It is determined on a standard ram impact machine (Fig. 191) which consists of two parallel rails between which a steel weight slides freely; various weights may be used in accordance with the standard (2.5 or 10 kg), depending upon the shock sensitivity of the substance being investigated. Under the load, there is a steel plate on a strong base. The device in which the shock sensitivity is determined (Fig. 192) is installed on the plate. For liquid-explosive tests, the device consists of a deep-bottom female die and a steel hammer. A weighed portion of the substance, normally about 0.03 g is placed into the die.

For testing solid explosives, a standard device of another design is used.

The solid materials are located on an anvil, in powder form; liquids may be tested in drop form. When the weight strikes the hammer of the device, depending upon the force of the stroke, an explosion does or does not occur. The minimum height for which explosions occur 100% of the time, and the maximum height for which misfires occur 100% of the time are taken to characterize the sensitivity of the material to
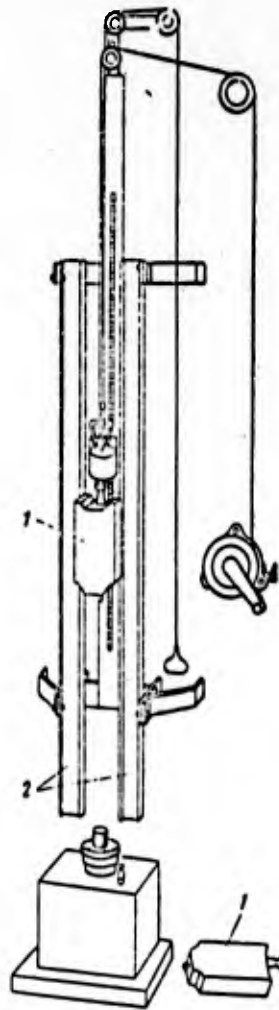
Fig. 191. Ram impact machine for
investigating shock sensitivity
of explosives. 1) Weight; 2)
guide rails.

shock; the height for which explosions occur 50% of the time and mis-
fires 50% of the time for a given weight is also taken as a character-
istic. A graph is plotted in order to determine the shock sensitivity.
On the axis of ordinates is plotted the height of the weight or the
work of the falling load (kgfm), and on the axis of abscissas — the
percent of explosions. No less than six determinations are made for
each point.

The shock sensitivity is not an accurate physical characteristic,
but is chiefly of value in comparisons. In this connection, when new
substances are tested for shock sensitivity on a ram-impact machine,
the results obtained are compared with the shock sensitivity of well-
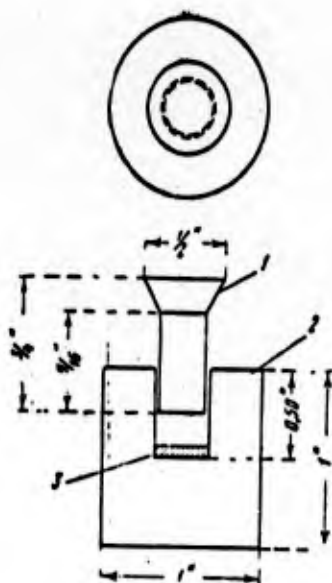
Fig. 192. Device for determining shock sensitivity of monopropellants and liquid explosives. 1) Piston; 2) well; 3) explosive.

known explosives. Trinitrotoluene, tetryl, and nitroglycerine are taken as standards.

Liquid monopropellants, which may be considered relatively safe when examined under laboratory conditions, are less shock-sensitive than trinitrotoluene in transport and storage.

Explosives may be classified according to shock susceptibility.

Table 144 gives the sensitivity characteristics for explosives and monopropellants by class.

Friction sensitivity, as in the case of shock sensitivity, characterizes the explosion hazard of a monopropellant.

In the simplest case, the friction sensitivity is determined in a porcelain mortar. A better method is to determine the friction sensitivity with a special friction device.

TABLE 144

Sensitivity Characteristics of Solid Explosives Compared with Monopropellant [1, 4]

1 Класс чувствительности ВВ	2 Общая характеристика	3 Высота падения груза 2 кг, при которой происходит взрыв, см	4 Примеры взрывчатых веществ	5 Примеры жидких однокомпонентных топлив
I	Весьма опасны в обращении [6]	2—3	Гремучая ртуть [7]	80—90%-ная перекись водорода + спирт [8]
		3—4	[9] Нитроглицерин	Тетранитрометан + бензол [10]
II	[11] Сравнительно безопасны в обращении	12—20	[12] Пироксилин	
III	Безопасны в обращении, при перевозке и хранении [13]	35—90	[14] Тринитрофенол	Азотная кислота + дихлорэтан [15]
		40—65	[16] Тетрил	Нитрометан [16a]
		60—160	Тротил [17]	
IV	Безопасны и не проявляют свойств обычных ВВ; детонируют только в особых условиях [18]	120—130	Динитробензол [19]	Жидкие однокомпонентные топлива низкой теплопроизводительности [20]
		170—180	Динитронафталин [21]	

1) Sensitivity class of explosive; 2) general characteristics; 3) height through which 2-kg weight must fall to produce explosion, cm; 4) examples of explosives; 5) examples of liquid monopropellants; 6) very dangerous to handle; 7) mercury fulminate; 8) 80-90% hydrogen peroxide + alcohol; 9) nitroglycerin; 10) tetranitromethane + benzene; 11) comparatively safe to handle; 12) pyroxylin; 13) safe to handle, store, and transport; 14) trinitrophenol; 15) nitric acid + dichloroethane; 16) tetryl; 16a) nitromethane; 17) trotyl; 18) safe; normal properties of explosives not manifested; detonates only under certain conditions; 19) dinitrobenzene; 20) low-heating-value liquid monopropellants.

c) Determining the liability of monopropellants to explosive decomposition upon rapid compression

Bubbles of air or gas can always form in a liquid monopropellant. Upon sharp compression of the fluid, owing to the increased pressure or hydraulic shock in flowing through piping, these bubbles will in turn be compressed; a rapid compression of a gas is always accompanied by a temperature rise, which may cause the propellant to ignite spontaneously. Thus, the presence of gas bubbles in contact with a monopropellant in fuel lines or in a tank may, in conjunction with a sharp pressure rise due to mechanical shocks or valve operation, be responsible

for explosive decomposition of a monopropellant. In this connection, it is necessary to allow for monopropellant sensitivity to a sharp rise in pressure. To do this, an installation has been developed to evaluate the sensitivity of monopropellants to a sharp pressure rise. This installation includes a device which permits nearly instantaneous application of high pressure to a specimen of monopropellant in contact with a gas bubble. The installation is provided with apparatus for measuring the required parameters.

The propellant specimen containing the gas bubble is placed in a test chamber bounded on one side by a piston that sets up the pressure, and on the other side by a burst diaphragm. The chamber is held at a given low or elevated temperature in a thermostat. The burst diaphragm, which is 2.54 mm thick, deforms during the experiment or ruptures in the presence of a detonation. The magnitude of the diaphragm's deformation is used to determine the pressure developed in the chamber.

The chamber has a volume of 1.3 ml; propellant specimens having volumes ranging from 0.2 to 1.1 ml may be located in the chamber; they may be placed in contact with gas bubbles of from 0.2 to 0.9 ml.

It is assumed that a monopropellant decomposes upon rapid compression as a result of local heating due to the nearly adiabatic compression of the gas bubble; as a consequence, the gas is heated to a high temperature. It is very probable that the high temperature is also responsible for decomposition of the propellant. When the temperature becomes sufficiently high, the propellant begins to break down and to liberate a considerable amount of heat, which facilitates rapid propagation of the reaction over the entire volume.

As experiments have shown, the sensitivity of a monopropellant when compressed in the presence of propellant vapors is far less than in the presence of air bubbles. This may be explained by the fact that

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propellant vapors, on the one hand, may condense rapidly when compressed, while on the other hand, the oxygen of the air leads to the initiation of an oxidation reaction in the propellant at elevated temperatures.

If we neglect heat losses over small time intervals, the temperature of an ideal gas upon adiabatic compression may be determined as follows:

$$\left(\frac{p_i}{p_0}\right)^{\frac{k-1}{k}} = \frac{T_i}{T_0}.$$

from which it follows that the maximum temperature developing upon compression of a bubble is determined, for equal values of $\underline{k}$ and T, by the size of the bubble.

The work of adiabatic compression (the energy applied to the piston) is connected with the temperature upon gas compression as follows:

$$W = \frac{n_g R_0 T_0}{k-1}\left(1 - \frac{T_i}{T_0}\right) \text{ kgfm.}$$

The installation mentioned above has been used to determine the sensitivity of four monopropellants. Bubble volume during the tests amounted to 0.2, 0.4, 0.6, and 0.8 ml. The tests determined the minimum energy that had to be supplied to the compression process in order to cause breakdown of the fuel.

Tests were made on n-propylnitrate, nitromethane, a mixture consisting of 60% ethyl nitrate and 40% propylnitrate, methylacetylene, hydrogen peroxide, hydrazine, dimethylhydrazine, and ethylene oxide. The measure of sensitivity was taken to be the minimum compression energy per unit volume of air bubble needed for explosive decomposition of the propellant. The results obtained are given below.

Propellant	Sensitivity, kgf·cm/ml
Ethyl nitrate – 60%.................	} 4.0 ± 0.8
Propyl nitrate – 40%...............	
Propyl nitrate.....................	6.7 ± 1.2
Nitromethane.......................	10.4 ± 1.7
Methylacetylene....................	86.0 ± 12
Hydrogen peroxide..................	144
Hydrazine..........................	144
Unsymmetric dimethylhydrazine......	144
Ethylene oxide.....................	144

Hydrogen peroxide, hydrazine, dimethylhydrazine, and ethylene oxide did not decompose under the worst experimental conditions over the $-20°$ to $+20°$ temperature range with 115 kgf·cm/ml of energy supplied, and an air-bubble volume of 0.8 ml.

d) Determining the susceptibility of monopropellants to explosive reaction

A monopropellant should provide for safe operation of the motor; it is thus necessary to have a propellant that is not liable to explosion or detonation under operating conditions.

Certain methods are known for determining the liability of explosive systems to detonation and the characteristics of the explosive power; they may be used to evaluate a monopropellant. As a rule, the so-called brisance test is employed; brisance characterizes the power and shattering effect of an explosion.

In the standard test, 50 g of the explosive or monopropellant is placed in a beaker 40 mm in diameter, which contains a standard No. 8 detonator cartridge [1, 2]. For powdered materials, a paper container is used and for liquids (i.e., monopropellants), a glass beaker with a top which has a channel for the detonator cartridge. The beaker with the material is placed on a steel plate 41.5 mm in diameter and 10 mm thick, which lies upon a lead column 40 mm in diameter and 60 mm high.
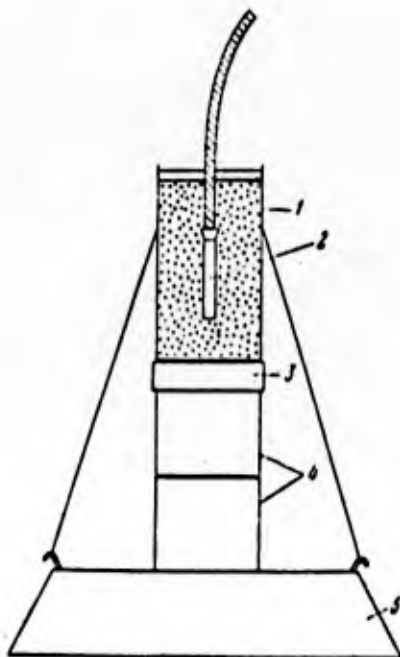
Fig. 193. Device for studying
brisance of sample and liabil-
ity to explosion. 1) Beaker
with explosive; 2) detonator;
3) steel plate; 4) lead col-
umns; 5) steel plate.

The column is installed on a massive steel plate (Fig. 193).

Upon detonation of the charge with the aid of the detonator car-
tridge from a Bickford fuse or electrical fuse, the substance explodes,
and the lead column is compressed, normally by 8-25 mm. If the sub-
stance under investigation was not exploded by the cartridge, the re-
sulting compression is due solely to the explosion of the cartridge,
and will not exceed 1-2 mm.

The compression of the lead column is used to indicate the occur-
rence of an explosion and as a measure of its power. The experiment is
repeated several times. If no explosion occurs, the experiment is re-
peated at least four times in order to make sure that the substance is
not subject to detonation.

Explosive systems that are not susceptible to detonation from a
No. 8 cartridge may be considered to be quite free of explosion hazard
in handling, storage, and transportation. Explosive compounds and liq-

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uid mixtures having heating values greater than 1200 kcal/kg most frequently produce a very large compression and deformation of the column, which complicates the measurement. Substances that do not explode under these test conditions as a result of the action of the detonator cartridge are safe under storage and transportation conditions, although this does not represent a complete characterization of such materials.

Although trinitrotoluene is detonated by the detonator cartridge, it is safe to handle, and a stoichiometric mixture of hydrogen peroxide and ethyl alcohol, which can be detonated by the cartridge, is very sensitive to shock and friction, and explodes easily from random jolts.

A monopropellant that is not exploded by the detonator cartridge is tested under the conditions mentioned by means of a No. 8 cartridge with an additional detonator in the form of a 10-g grain of tetryl, which provides a powerful explosive impulse. A separate experiment is used to determine the compression created by the tetryl grain with the detonator cartridge, in which the beaker is filled with an inert substance above which the detonator with the tetryl grain is exploded. The compression obtained is subtracted from the compression found upon explosion of the substance under investigation.

Monopropellants that do not detonate when the 10-g tetryl grain is used are quite safe under ordinary conditions of use, i.e., they are insensitive to shock, friction, and small-arms fire.

A more severe test for liability to detonation is the explosion of a monopropellant in a steel tube 30-40 mm in diameter, using a 10-g tetryl grain, since the strong jacket is favorable to the propagation of detonation [5]. The nature of damage to the tube is an indication of susceptibility to explosion and detonation.

The results obtained depend to a considerable measure upon the experimental conditions. Thus, given a strong tube and a powerful

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priming charge, the propagation of an explosion will be more probable
than in a thin-walled tube.
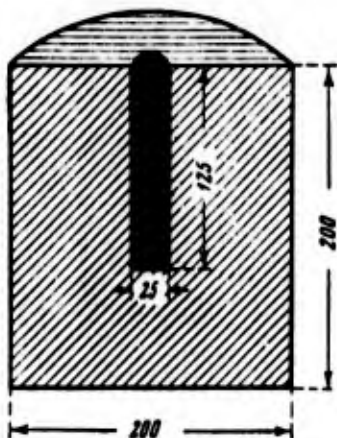
Fig. 194. Testing an explosive
for fugacity (lead bomb prior
to explosion).

Fig. 195. Lead bomb after ex-
plosion in fugacity test.

Some substances produce a small compression (3-6 mm) upon testing
for brisance with an additional tetryl grain, but a detonation does
not propagate in tubes. In this case, explosion of the layer of sub-
stance adjacent to the detonator is not strong enough to cause explo-
sive decomposition of the succeeding layers of the substance, i.e.,
the explosive reaction is not selfpropagating.

In many cases, the liability of a substance to explosive decompo-
sition is characterized by the results of a test in a lead bomb [3].

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The substance, weighing 10 g, is introduced into a channel in the lead bomb. A sand plug is placed above the material, or it is compressed by a steel plunger with an opening. The substance is exploded by means of a detonator cartridge under these closed-space conditions (Figs. 194, 195). The expansion of the lead channel serves to indicate that there has been an explosion, and as a measure of its power. This test is called a fugacity test, and is characterized by the expansion of the interior channel of the lead bomb, expressed in cubic centimeters.

e) Rate of combustion

The rate of combustion is an important characteristic of a solid monopropellant (powder) where it is necessary to know the rate of combustion as a function of the pressure and temperature in order to properly set up the powder combustion process in the motor.

With a liquid monopropellant, the combustion rate cannot be utilized directly in motor design, since the combustion process in a ZhRD
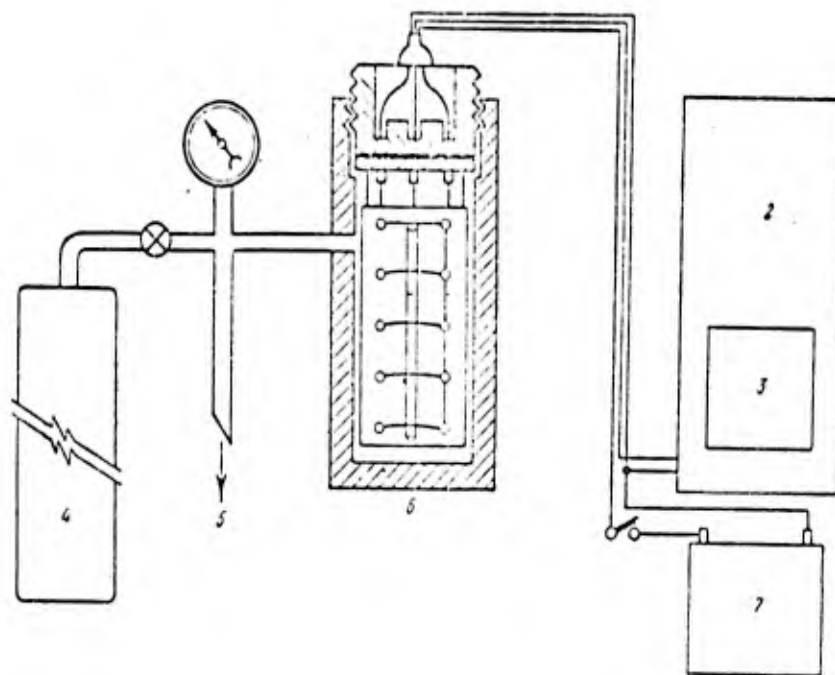
Fig. 196. Installation for investigating combustion rate of monopropellants under pressure. 1) Pressure gauge; 2) oscillograph; 3) chamber; 4) equalizing cylinder with nitrogen; 5) pressure escape; 6) bomb; 7) battery.

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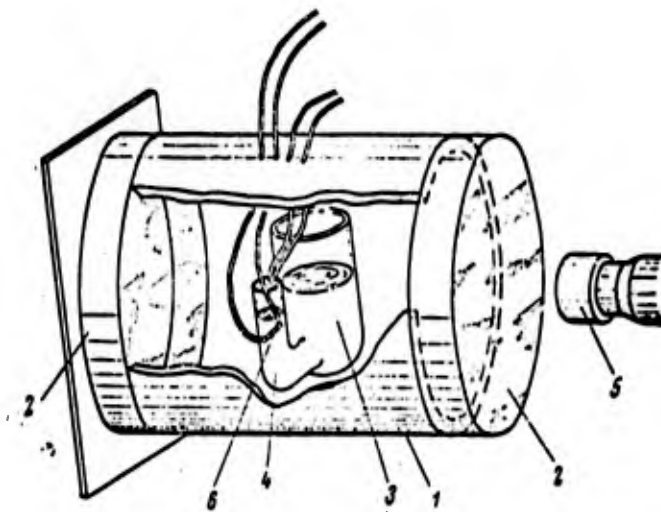
Fig. 197. Diagram of installation for investigating combustion rate of liquid monopropellants with high-speed photographic process. 1) Housing; 2) heavy glass window; 3) propellant reservoir in the form of coupled vessels; 4) tube for ignition; 5) high-speed camera; 6) thermocouple.

is extremely complex. In this case, however, it is also desirable to have an idea of the rate and stability of combustion. Many investigations into the combustion rates of liquid monopropellants have been published.

The installation used to study the combustion rate of rocket monopropellants consisting of nitric acid and nitroparaffins under pressure is shown in Fig. 196 [5].

A glass tube is located in the bomb 6; it is filled with liquid propellant. The required pressure in the bomb is set up with the aid of the compressed-nitrogen cylinder 4; the pressure is maintained at the predetermined level with the aid of a tank receiver. The pressure is recorded by the pressure gauge 1. Battery 7 is used for hot-wire ignition of the fuel by igniting the cordite powder which sets off the basic substance. The combustion rate is recorded with the aid of low-melting wires which are spaced 50 mm apart in the glass tube containing the substance; the tube is 180 mm long and 5 mm in diameter. A cur-

rent of 300 ma is passed through the wires. Interruption of an electrical circuit is recorded by a sensitive galvanometer connected to a multichannel oscillograph, which makes it possible to determine the motion of the flame front. The photographic paper carries time pips. At the same time, electronic timers show the time at which the first and succeeding wires were broken. The bomb also has a narrow slot covered with thick glass through which it is possible to photograph the entire combustion process.

A diagram of a similar installation is given in Fig. 197 [6], and the results of the experiments in Section 2 of this chapter.

2. Propellants Based upon Nitric-Acid Solutions

Nitric acid is a very reactive substance, and thus there are only a few compounds that will dissolve in nitric acid without chemical reaction. These compounds include nitro derivatives and certain chlorine derivatives. Alcohols, aldehydes, ketones, and ethers will dissolve in nitric acid, but only to the accompaniment of vigorous nitration and oxidation.

Solutions of organic compounds in nitric acid have found employment as liquid explosives, and under certain conditions and for specific compositions may also be considered as ZhRD propellants.

Table 145 shows recipes for well-known liquid explosives.

Solutions of nitro derivatives in nitric acid and oxides of nitrogen are characterized by high heating values of the order of 1400-1500 kcal/kg and a significant sensitivity to shock. Mixtures based upon oxides of nitrogen are especially sensitive to shock; they are so dangerous that they are prepared directly before use.

Mixtures consisting of nitric acid and aromatic nitro derivatives are not as dangerous to handle as mixtures based upon oxides of nitrogen. In standard reaction engines, however, they cannot be used since

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TABLE 145

Liquid Explosives Based upon Nitric Acid and Oxides of Nitrogen [1-4, 7, 8]

1 Название	2 Компоненты	3 Содержание, %	4 Теплопроизводительность, ккал/кг	5 Скорость детонации, м/сек	6 Область применения
7 Гельгофит	$C_6H_5NO_2$ HNO_3	28 72	1470	—	—
8 Геллит	$C_6H_5NO_2$ $(CH_3)_2C_6H_3NO_4$ HNO_3		1400	6700	Авиабомбы 14
9 Оксонит	$(NO_2)_3C_6H_2OH$ HNO_3	58 42	1550	—	—
10 Гельгофит	$C_6H_4(NO_2)_2$ HNO_3	40 60	1500	—	—
11 Раствор нитрометана в азотной кислоте	CH_3NO_2 HNO_3	61,8 38,2	1530	—	—
12 Панкластит . . .	13 Бензин N_2O_4	21} 79}	1750	1710	—
»	$C_6H_5NO_2$ N_2O_4	35} 65}	1710	7650	Авиабомбы 14
»	CS_2 N_2O_4	29} 71}	1590	—	Авиабомбы 14.

1) Name; 2) components; 3) content, %; 4) heating value, kcal/kg; 5) detonation rate, m/sec; 6) field of application; 7) gel'gofit; 8) gellit; 9) oxonite; 10) tel'gofit; 11) solution of nitromethane in nitric acid; 12) panclastite; 13) gasoline; 14) aerial bombs.

combustion may turn into detonation.

Table 146 shows the shock sensitivity of liquid explosive mixtures in comparison with standard explosives.

The lowest shock sensitivity is possessed by a solution of dichloroethane in nitric acid. This liquid explosive mixture can be considered safe in handling and transport. A stoichiometric mixture of dichloroethane with nitric acid is not susceptible to explosion from a standard detonator cartridge. An added detonator, however, will produce an explosion. This mixture burns calmly when ignited in open containers holding several liters. This is still no guarantee that explosion cannot occur when the mixture is used in reaction engines under all operating conditions.

Sensitivity to Shock for Certain Liquid Explosives of Monopropellants [1, 4]

1 Название	2 Компоненты	3 Содержание, %	4 Темп. вспышки, °C	5 Процент взрывов, полученный при падении груза 10 кг с высоты 100 см
6 Дихлорэтан + азотная кислота	$C_2H_4Cl_2$ HNO$_3$	60 40	350 360	—
7 Тринитротолуол	$C_6H_2(NO_2)_3CH_3$	—	—	17
8 Пикриновая кислота . .	$C_6H_2(NO_2)_3OH$	—	—	50
9 Гельгофит	$C_6H_5NO_2$ HNO$_3$	28 72	390	90
10 Оксонит	$C_6H_2(NO_2)_3OH$ HNO$_3$	58 42	—	95
11 Дихлорэтан + азотная кислота	$C_2H_4Cl_2$ HNO$_3$	50 50	—	25 (высота падения 145 см) [12]
13 Нитрометан	CH_3NO_2	—	260°	
14 Нитрометан + азотная кислота	CH_3NO_2 HNO$_3$	62 38	300 —	0 (высота падения 50 см) [15] 5 (то же) [16] 5 (то же) [16]

1) Name; 2) components; 3) content, %; 4) flash point, °C; 5) percent of explosions upon dropping 10-kg weight from height of 100 cm; 6) dichloroethane + nitric acid; 7) TNT; 8) picric acid; 9) gel'gofit; 10) oxonite; 11) dichloroethane + nitric acid; 12) (from 145-cm height); 13) nitromethane; 14) nitromethane + nitric acid; 15) (from height of 50 cm); 16) same.

Liquid explosive mixtures based upon solutions of aromatic nitro compounds in nitric acid are more shock-sensitive than trinitrotoluene.

When aromatic mononitro compounds, such as nitrobenzene, are dissolved in nitric acid, the benzene nitrates to dinitrobenzene. This is connected with the considerable heating of the mixture which thus requires good cooling.

A liquid monopropellant may be obtained by dissolving in nitric acid of such solid polynitro compounds as dinitrobenzene, picric acid and trinitrotoluene. A drawback to such a monopropellant is the fact that when the nitric acid evaporates, the remaining polynitro compound is sensitive to shock or friction.

In order to avoid corrosion of steel by nitric acid, 5-10% of sulfuric acid may be added to the mixture.

A solution of ammonium nitrate in ammonia is a noteworthy example

of a monopropellant consisting of a solution of an inorganic combustible in an inorganic oxidizer. This is a very interesting system which is a liquid for a 30-40% NH_3 content, and freezes at -40°, while with an 85% content of NH_4NO_3 in 15% NH_3, it is a solid, melting at $+70^\circ$.

The stoichiometric composition, calculated for complete combustion, is 87.5% NH_4NO_3 and 12.5% NH_3. The system containing 75% ammonium nitrate and melting at 0° corresponds to a specific impulse of 175 sec with $p/p_0 = 20$.

3. Propellants Based upon Nitromethane and Nitro Ethers

Of the nitro compounds, only nitromethane presents any interest at present as a monopropellant.

Nitromethane is a liquid, and has a relatively high heating value. It is relatively immune to shock or friction. Low-molecular-weight nitro ethers are very sensitive to shock and friction, and cannot be used in pure form. Tables 147 and 148 show the properties of certain liquid nitro compounds and nitro ethers.

TABLE 147

Properties of Certain Nitro Compounds and Nitro Ethers [4, 9]

1 Соединение	2 Формула	3 Теплопроизводительность, ккал/кг	4 Чувствительность к удару (высота падения груза 2 кг), см
5 Динитрогликоль	$C_2H_4(ONO_2)_2$	1581	20—25
6 Нитроглицерин	$C_3H_5(ONO_2)_3$	1485	4—8
7 Метилнитрат . .	CH_3ONO_2	1490	40
8 Этилнитрат . .	$C_2H_5ONO_2$	713	—
9 Нитрометан . .	CH_3NO_2	1040	Мало чувствителен 10
11 Нитроэтан . .	$C_2H_5NO_2$	680	Практически 12 нечувствителен

1) Compound; 2) formula; 3) heating value, kcal/kg; 4) shock sensitivity (2-kg-weight drop height), cm; 5) dinitroglycol; 6) nitroglycerin; 7) methyl nitrate; 8) ethyl nitrate; 9) nitromethane; 10) not very sensitive; 11) nitroethane; 12) practically insensitive.

TABLE 148

Flash Point of Nitro Ethers for
Various Induction Periods [10]

1 Вещество	2 Температура вспышки (° C) при задержке	
	5 сек.3	10⁻⁹ сек. 3
4 Метилнитрат	269	435
5 Этилнитрат	254	325
6 Пропилнитрат	247	331
7 Динитрат гликоля . . .	238	357

1) Substance; 2) flash point (^{O}C)
for lag of; 3) sec; 4) methyl nit-
rate; 5) ethyl nitrate; 6) propyl
nitrate; 7) glycol dinitrate.

Dinitroglycol and nitroglycerin have high heating values, but are
very sensitive to shock and thus dangerous to handle. Combustion of
these nitroethers easily changes to detonation.

Methyl nitrate is considerably less shock-sensitive than nitro-
glycol or nitroglycerin. In this respect, they are similar to hexogen —
an explosive used for munitions. Methyl nitrate, however, is more sen-
sitive than nitro compounds. Thus, it detonates upon ignition from a
Bickford fuse in a closed space. Methyl nitrate is an exceptionally
powerful explosive, detonating at a rate of 8000 m/sec.

In Germany, a monopropellant based upon methyl nitrate has been
tested [9]; it consists of 30% CH_3OH and 70% CH_3ONO_2, with a heating
value reaching 1000 kcal/kg.

Nitromethane presents considerable interest as a monopropellant.
Nitromethane is a liquid explosive with a negative oxygen balance. Its
decomposition reaction, accompanied by the evolution of 1030 kcal/kg,
may be written as follows:

$$CH_3NO_2 \rightarrow CO + H_2O + \tfrac{1}{2}H_2 + \tfrac{1}{2}N_2.$$
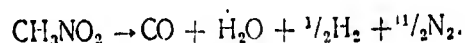
Accurate thermodynamic calculations yield the following equation
corresponding to equilibrium composition at a combustion temperature

of $2450^{\circ}K$:

$$CH_3NO_2 \rightarrow 0.2\,CO_2 + 0.8\,CO + 0.8H_2O + 0.7\,H_2 + 0.5\,N_2,$$
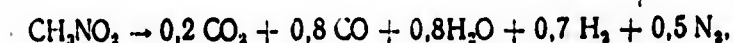
and corresponding to a specific impulse of 210 sec at $p/p_0 = 25$, with heating value of 1070 kcal/kg.

Nitromethane is a low-sensitivity explosive. It is not detonated by a standard detonator cartridge, does not explode in heavy steel tanks ejected from aircraft, but does detonate in thin-walled steel tubes when set off with the aid of large charges of tetryl.

Inadequate treatment is given in the literature to the shock sensitivity of nitromethane in comparison with other explosives. In flowing through tubes, nitromethane may explode under a sudden application of pressure of the order of 140 kgf/cm^2.

If the tube is closed at one end, an explosion may occur with a hydraulic shock of 60 kgf/cm^2. Explosion may evidently be facilitated by contraction of tubes, nozzles, and other obstacles, if the material is flowing out under high pressure.

Nitromethane is stable at temperatures of from $20-50^{\circ}$, and may be stored and transported safely in 200-liter steel tanks.

Explosion did not occur when rifle bullets were fired through iron tanks with nitromethane. However, when heavy-caliber 12.5 mm machine gun bullets were fired, the nitromethane was observed to explode. No explosion resulted when tracer bullets were used. Incendiary bullets, however, produced explosions and ignition in all cases.

The combustion of nitromethane in air proceeds quietly and detonation does not occur.

The technical product contains 95-96% nitromethane and 4-5% nitroethane, nitropropane, and oxidation products. Nitromethane containing almost no impurities may be obtained by purifying the technical product. Table 149 shows the properties of technical and purified nitro-

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TABLE 149

Properties of Technical and Purified Nitromethane

| Температура, °C | 95%-ный CH₃NO₂ | | 100%-ный CH₃NO₂ | |
1	удельный вес при 20°	вязкость, при 20°, сст	удельный, вес при 20°	вязкость при 20°, сст
10	1,140	.0,749	1,149	0,743
25	1,120	0,625	1,128	0,625
40	1,100	0,533	1,108	0,533

1) Temperature, ^{O}C; 2) specific gravity at 20°;
3) viscosity at 20°, centistokes.

methane.

Nitromethane is utilized in experimental reaction engines as a monopropellant, and in conjunction with oxidizers: oxygen and hydrogen peroxide. It is necessary to add combustion catalysts to nitromethane where it is used alone in order to obtain complete combustion. These catalysts are nitromethane-soluble salts of chromium, cobalt, copper, nickel, lead, and manganese. Especially favorable results are given by chromium acetylacetonate $Cr(C_5H_7O_2)_3$ which dissolves in nitromethane to a concentration of about 2%. Chromium acetylacetonate is prepared by heating acetylacetone with ammonia and chromium nitrate. The shock sensitivity of nitromethane is increased somewhat by chromium and cobalt salts, and lowered by nickel and copper salts.

Numerous experiments have been carried out with technical 96% nitromethane. It has been established that the addition of 4-10% of gasoline, methanol, and other organic solvents decreases, but does not eliminate completely, the tendency of nitromethane to detonation.

Experiments with nitromethane in reaction engines have shown that for combustion stability it is desirable to employ nitromethane in combination with oxygen or hydrogen peroxide. In this case, there is no need for combustion catalysts. Reliable ignition of the propellant is of especially great importance in preventing detonation of nitromethane

in a motor, since a large ignition lag may lead to an explosion. In order to provide for complete combustion of nitromethane in the absence of an oxidizer, it is necessary to have a motor pressure of the order of 38.5 kgf/cm^2. If the nitromethane is employed in combination with hydrogen peroxide, combustion occurs at lower pressure. In this case, the propellant may be ignited by means of catalytic dissociation of the hydrogen peroxide by permanganate.

Table 150 gives the working characteristics of a propellant based upon nitromethane and several oxidizers.

TABLE 150

Working Characteristics of Nitromethane-Base Propellants [9, 10]

1 Топливо	2 Содержание компонентов, %	3 Теплопроизво-дительность, ккал/кг	4 Скорость ис-течения, м/сек	5 Удельный импульс, сек
6 Нитрометан	100	1030	1780	182
7 Нитрометан	61,8			
8 Азотная кислота .	38,2	1538	2170	222
7 Нитрометан	52			
9 90%-ная перекись водорода	48	1500	2140	218
7 Нитрометан	71,6			
10 Кислород	28,4	1820	2370	242
7 Нитрометан	90			
11 Толуол	10	920	1690	173
7 Нитрометан	80			
11 Толуол	20	820	1600	163

1) Propellant; 2) component content, %; 3) heating value, kcal/kg; 4) exhaust velocity, m/sec; 5) specific impulse, sec; 6) nitromethane; 7) nitromethane; 8) nitric acid; 9) 90% hydrogen peroxide; 10) oxygen; 11) toluene.

As has been shown above, a nitric acid-nitropropane system has been studied as a monopropellant. Nitropropane is obtained by nitration of propane with 53-67% nitric acid at 400°. In this process, in addition to normal nitration, destructive nitration occurs as a result of partial cracking and oxidation of the propane. Thus, technical nitropropane is a mixture of nitro compounds, having the composition: nit-

romethane, 9%, nitroethane, 26%, 1-nitropropane, 32%, and 2-nitropropane, 43%. The isomers of nitropropane are separated from this mixture by distillation.

A mixture of 80-90% nitroethane and 10-20% nitromethane is obtained upon nitration of ethane. A more complicated mixture is formed upon nitration of n-butane [11].

The physicochemical properties of certain low-molecular-weight nitroparaffins are shown in Table 151.

TABLE 151

Physicochemical Properties of Nitroparaffins [12]

1 Соединение	2 Плотность при 25°	n_D^{20}	3 Т. пл., °С	4 Динамическая вязкость при 20°,сантипуазы.
5 Нитрометан	1,1286	1,3818	—29	0,632
6 Нитроэтан	1,0413	1,3917	—	0,661
7 1-Нитропропан	0,9934	1,4018	—	0,798
8 2-Нитропропан	0,9821	1,3944	—93	0,750
9 1-Нитробутан	0,9685	1,4108	--	0,931
10 2-Нитробутан	0,9609	1,4044	—132	0,878
11 1,1-Динитропропан	1,2610	1,4339	—42	2,535
12 2,2-Динитропропан . . .	1,3000	—	53	—
13 1,3-Динитропропан . . .	1,3540	1,4654	—20	—
14 Тринитрометан	1,6150	1,4454	25	—.

1) Compound; 2) density at 25°; 3) melting point, °C; 4) dynamic viscosity at 20°, centipoises; 5) nitromethane; 6) nitroethane; 7) 1-nitropropane; 8) 2-nitropropane; 9) 1-nitrobutane; 10) 2-nitrobutane; 11) 1,1-dinitropropane; 12) 2,2-dinitropropane; 13) 1,3-dinitropropane; 14) trinitromethane.

Table 152 shows the thermochemical properties of nitroparaffins.

An investigation of the combustion rate for stoichiometric mixtures of 2-nitropropane with 98% nitric acid in a bomb (Fig. 198) showed that combustion is supported at a pressure of 10 atm [13]. At 100 atm, the combustion rate of the mixture in glass tubes 7 and 8 mm in diameter is independent of the diameter. In 6- and 5-mm diameter tubes, however, the combustion rates are 15 and 40% less, respectively.

TABLE 152

Thermochemical Properties of Nitroparaffins [12]

1 Соединение	2 Теплота образования при 25°, ккал/моль	3 Теплотворная способность *		6 Скрытая теплота испарения, ккал/кг
		4 ккал/моль	5 ккал/кг	
7 Нитрометан	21,28	175,87	2881	9,09
8 Нитроэтан	33,48	325,79	4340	9,94
9 1-Нитропропан	40,05	481,33	5403	10,37
10 2-Нитропропан	43,78	477,60	5361	9,88
11 1-Нитробутан	46,03	637,47	6182	11,61
12 2-Нитробутан	49,61	633,89	6147	10,48
13 1,1-Динитропропан	40,78	447,65	3338	14,93
14 1,3-Динитропропан	53,51	434,92	3243	—
15 2,2-Динитропропан	44,87	443,56	3008	—
16 Тринитрометан	18,63	112,62	746	—
17 Тетранитрометан	—	—	543	—
18 2,3-Диметил-2,3-динитробутан	—	—	5110	—
19 2,2-Диметил-1,3-динитропропан	—.	—	4606	—
20 1,1,1-Тринитроэтан	—	—	1777	—
21 2-Метил-2,3,3-тринитробутан	—	—	3381	—
22 2-Метил-2,3,3-тринитропентан	—	—	3944	—
23 2,2,3,3-Тетранитробутан	—	—	2460	—

*The heating value is found by combustion in a bomb calorimeter in oxygen.

1) Compound; 2) heat of formation at 25°, kcal/mole; 3) heating value; 4) kcal/mole; 5) kcal/kg; 6) latent heat of vaporization, kcal/kg; 7) nitromethane; 8) nitroethane; 9) 1-nitropropane; 10) 2-nitropropane; 11) 1-nitrobutane; 12) 2-nitrobutane; 13) 1,1-dinitropropane; 14) 1,3-dinitropropane; 15) 2,2-dinitropropane; 16) trinitromethane; 17) tetranitromethane; 18) 2,3-dimethyl-2,3-dinitrobutane; 19) 2,2-dimethyl-1,3-dinitropropane; 20) 1,1,1-trinitroethane; 21) 2-methyl-2,3,3-trinitropentane; 22) 2-methyl-2,3,3-trinitropentane; 23) 2,2,3,3-tetranitrobutane.

The combustion rate depends upon pressure. In the 14-70 and 70-140 atm pressure ranges, the slopes of the curves showing the length of the burning layer as a function of time differ considerably. This clearly indicates that there is a different reaction mechanism, depending upon pressure. Figure 199 shows the nature of the flame in the burning combustibles as a function of pressure [10].

The combustion rate of liquid ethyl nitrate, ethyleneglycol nitrate, and triethyleneglycol nitrate as a function of pressure and tem-
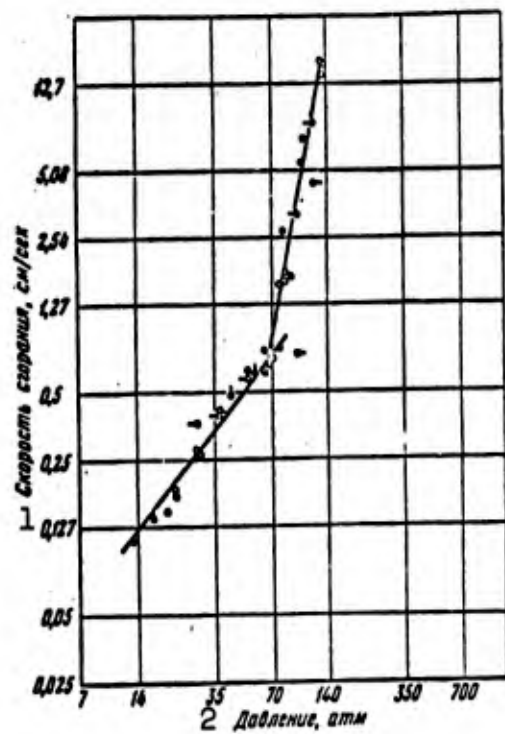
Fig. 198. Effect of pressure
upon combustion rate of stoi-
chiometric mixture of 2-nitro-
propane and nitric acid. 1)
Combustion rate, cm/sec; 2)
pressure, atm.
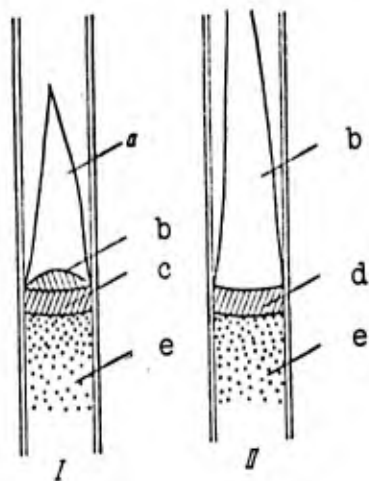
Fig. 199. Nature of flame in
propellant of 2-nitropropane
and nitric acid at pressures
of 40 and 80 atm. I) Pressure
of 40 atm; II) pressure of 80
atm; a) thin blue-white flame;
b) dense blue-white flame; c,
d) dense blue-white flame; e)
solution of nitropropane in
nitric acid.

perature, for various degrees of deuteration and purity, has been studied with the aid of high-speed photography [6] in a special chamber illustrated in Fig. 197.

It is curious that deuterated ethyl nitrate $C_2D_5ONO_2$ burns at a lower rate in all pressure ranges than does ordinary ethyl nitrate $C_2H_5ONO_2$ (Fig. 200). The same situation holds for ordinary and deuterated ethyleneglycol.

The effect of temperature and pressure on the combustion rate of triethyleneglycol nitrate $O_2NOCH_2CH_2OCH_2CH_2OCH_2CH_2ONO_2$ is shown in Fig. 201.

The flame propagation rates of methyl- and ethyl nitrates as vapors differ quite sharply. Vapors of methyl nitrate CH_3ONO_2 are characterized by an exceptionally high flame propagation rate (1345 cm/sec), which essentially corresponds to rates occurring in an explosion. The flame propagation rate in vapors of ethyl nitrate $C_2H_5ONO_2$ is only 35 cm/sec, which corresponds to the normal combustion rate of substances in the vapor state when mixed with oxidizers [14-16].

Figure 202 shows the variation in combustion rate for vapors of nitro ethers as a function of the mole proportion of ethyl nitrate to methyl nitrate.

Propyl nitrate $CH_3CH_2CH_2ONO_2$ is used as a monopropellant. In order to reduce gum formation, it is suggested that ferrocene $(C_5H_5)_2Fe$ be added to the propyl nitrate. A detonator cartridge will not detonate propyl nitrate in steel tubes 6.3, 12.7, and 31.7 mm in diameter. The autoignition temperature for n-propyl nitrate with air is 177°.

The combustion of propyl nitrate occurs with the formation of a large amount of gaseous products:

$$C_3H_7ONO_2 \rightarrow 3CO + 3\tfrac{1}{2}H_2 + \tfrac{1}{2}N_2.$$
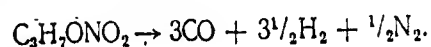
It is employed as a power source to run turbopumps.
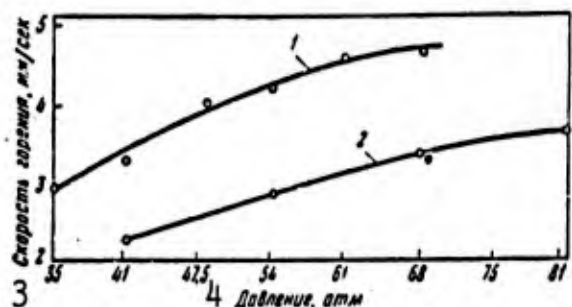
Fig. 200. Combustion rate of ethyl
nitrate and deuterated ethyl nitrate
as a function of pressure. 1) Ethyl
nitrate; 2) deuterated ethyl nitrate;
3) combustion rate, mm/sec; 4) pres-
sure, atm.
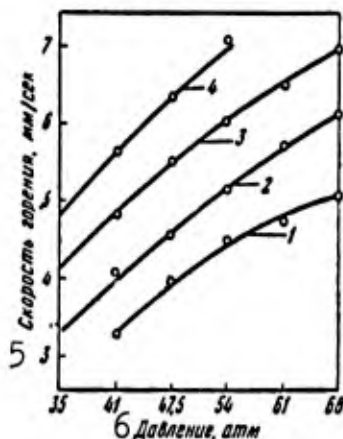
Fig. 201. Combustion rate of
triethyleneglycol dinitrate as
a function of temperature and
pressure. 1) 25°; 2) 50°; 3)
75°; 4) 100°; 5) combustion
rate, mm/sec; 6) pressure, atm.

In connection with the utilization of nitromethane as a rocket

monopropellant, its oxidation-thermal decomposition under pressure at

high temperatures has recently been studied.

This investigation is interesting in connection with the fact

that the propellant goes through several stages in a rocket motor, one

of which is accompanied by thermal-oxidation splitting.

Table 153 gives data on the thermal-oxidation decomposition of

nitromethane in time at various pressures.

In the presence of an oxidizer — oxygen — more complete thermal-
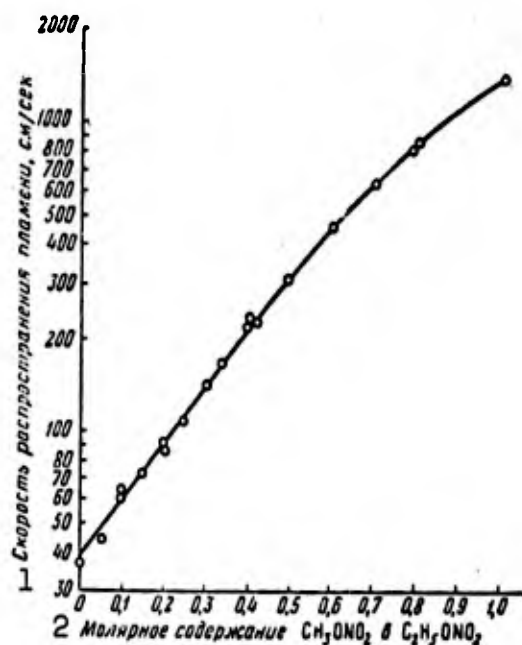
Fig. 202. Rate of propagation
of flame in ethyl nitrate vap-
ors mixed with methyl nitrate
vapors. 1) Flame propagation
rate, cm/sec; 2) mole content
of CH_3ONO_2 in $C_2H_5ONO_2$.

TABLE 153

Thermooxidation Decomposition of Nitromethane un-
der Pressure at 355° [15]
(Number of Moles of Products per Mole of Decompos-
ing Nitromethane x 100)

1)Давление, am	12.2	16	15	21	16	16 *
2)Время, мин.	2	5	15	31	24 часа 3	
4)Продукты:						
CO_2	8	19	20	31	34}	96
CO	17	20	18	12	19}	
CH_4	9	11	8	5	6	Следы 5
HCN	35	38	39	43	22	3,5
CH_3CN	5	1	3	4	9	—
CH_2O	6	3	1	—	—	—
NO	42	53	35	26	2	—
N_2O	2	2	7	3	—	—
N_2	4	2	6	10	35	—
H_2O	101	96	100	106	111	—

*Nitromethane with 16 mole-% of oxygen.

1) Pressure, atm; 2) time, min; 3) hours; 4) prod-
ucts; 5) traces.

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oxidation decomposition of nitromethane occurs.

Both extended reaction time and pressure facilitate an increase in the CO_2 content of the products of the incomplete reaction.

Clearly, hydrogen cyanide and nitric acid may be considered to be the chief intermediate reaction products from the breakdown of nitromethane and other nitro compounds in the preflame zone when they are burned in motors.

Thermal decomposition of nitromethane takes place at considerably greater speeds with elevated temperature. Thus, at 750°, 30% decomposition occurs after 0.13 millisec, and in 0.04 millisec at 800°.

4. Fuels Based upon Tetranitromethane

Tetranitromethane may be considered to be a monopropellant, since the reaction of intramolecular oxidation of tetranitromethane is accompanied by the liberation of a considerable quantity of heat:

$C(NO_2)_4 \rightarrow CO_2 + 3O_2 + 2N_2 + 102.9$ kcal/g-mole, or 526 kcal/kg.
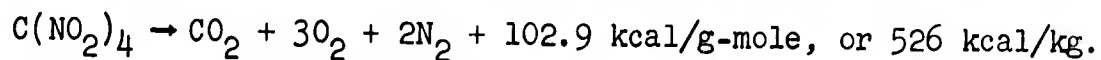
Pure tetranitromethane is not used alone as a propellant, however.

Tetranitromethane is an endothermic compound with a heat of formation of 8.9 kcal/g-mole. It begins to decompose at the boiling point of 126-127°.

Rot [17] has made a detailed investigation of the explosive properties of solutions of nitrobenzene in tetranitromethane.

The shock sensitivity was investigated in a special plunger-type device having a hammer diameter of 5.6 mm; an ampoule with the material was placed under the hammer. A blow with the hammer is produced by a weight of 2.15 or 5.04 kg, falling from various heights. The work of the blow was determined as the work in kgfm (i.e., the product of the weight by the height of the fall) per cm^2 of surface.

The height through which the weight fell and the work of the blow were recorded for the height at which 50% of 10 tests produced explo-

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TABLE 154

Explosive Properties of Solutions of
Nitrobenzene in Tetranitromethane [17, 18]

Концентрация раствора нитробензола в тетранитрометане, % [1]	Чувствительность к удару (работа удара), кГ м/см³ [2]	Скорость детонации, м/сек [3]	Фугасность, см³ [4]	Бризантность, мм [5]
5,0	4,80	6870	397	4,32
10,0	4,30	7030	534	4,50
15,0	4,30	7480	655	5,25
20,0	3,65	7550	832	5,43
20,5	5,15	7700	888	5,45
25,0	8,06	7575	840	5,66
30,0	8,06	7500	703	5,25
35,0	15,00	7220	627	5,20
40,0	15,00	7000	546	4,92
50,0	6 Отказ	6700	—	4,40
70,0	"	5800	315	3,20
80,0	"	6 Отказ	6 Отказ	6 Отказ

7 *Обычные взрывчатые вещества*

8 Нитроглицерин	4,75	7450	—	—
9 Тринитротолуол	11,1	7200	340	—

*From compression of copper column.

1) Concentration of solution of nitrobenzene in tetranitromethane, %; 2) shock sensitivity (work of shock), kgfm/cm^2; 3) rate of detonation, m/sec; 4) fugacity, cm^3; 5) brisance; 6) no explosion; 7) normal explosives; 8) nitroglycerin; 9) trinitrotoluene.

sions. The results of the tests are shown in Table 154.

Determinations were made of the detonation rate, the fugacity (from the expansion of a channel in a lead bomb), and the brisance (from the compression of a copper column in a standard test).

At concentrations of 5-10%, solutions of nitrobenzene in tetranitromethane have a sensitivity, under comparable experimental conditions, close to that of nitroglycerin, and at concentrations of 30-40%, close to that of tetryl.

Under similar conditions, trinitrotoluene produces a compression

of 4.2 mm; 5 and 40% solutions of nitrobenzene in tetranitromethane
have a greater brisance than does trinitrotoluene.

The fugacity of solutions of nitrobenzene in tetranitromethane
was determined in a lead bomb 200 mm in diameter and 250 mm high, with
an internal cylindrical channel 12.5 mm in diameter.

TABLE 155

Susceptibility and Explosive Effect of Tetranitro-
methane, its Mixtures, and Normal Explosives from
Volume of Depression in Plate (ml) [18]

№ детонато-ра [1] *	Тетранитро-метан [2]	$C (NO_2)_4 - 70\%$ $N_2O_4 - 30\%$	$C (NO_2)_4 - 67\%$ $C_6H_4 - 13\%$	Тринитрото-луол [3]	Нитроглицерин [4]
1	12	0	413	0	171
2	44	0	404	0	172
3	65	13	404	218	379
5	86	48	404	268	407
8	71	37	445	332	445

*According to German standard, the power rises
with ascending sequence number.

1) Detonator No.; 2) tetranitromethane; 3) trinit-
rotoluene; 4) nitroglycerin.
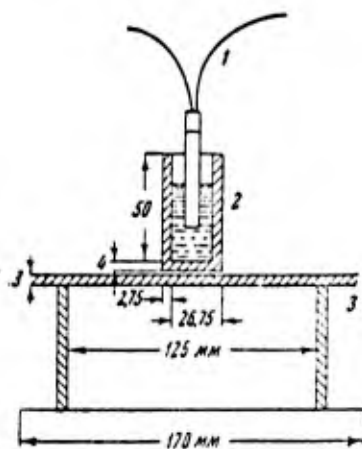
Fig. 203. Arrangement of in-
stallation for studying the ex-
plosive properties of solutions
of organic substances in tetra-
nitromethane. 1) Detonator; 2)
mixture; 3) plate.

A steel piston with an 8-mm aperture is pressed into the bomb chan-
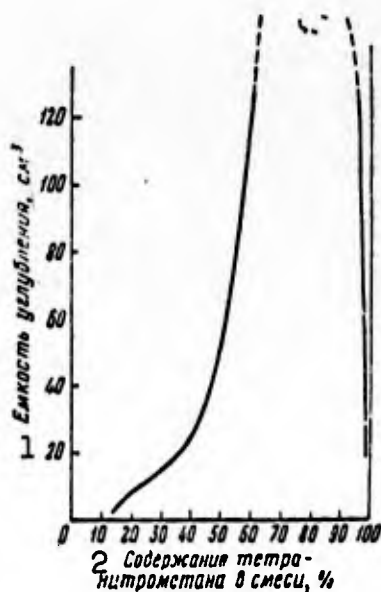
Fig. 204. Brisance of solutions
of hydrocarbons in tetranitro-
methane according to plate de-
formation. 1) Capacity of in-
dentation, cm^3; 2) content of
tetranitromethane in mixture, %.
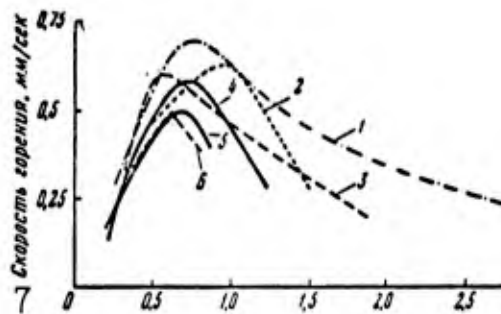
Fig. 205. Combustion rate for
mixtures of tetranitromethane
with alcohols. 1) n-Hexanol;
2) n-octanol; 3) n-butanol; 4)
n-propanol; 5) isopropanol; 6)
isobutanol. The axis of abscis-
sas shows the relationship to
the stoichiometric composition.
7) Combustion rate, mm/sec.

nel, after which 8.5 ml of solution is poured in. The substance is set

off by a detonator cartridge introduced through the hole in the piston.

The fugacity is determined from the expansion of the bomb following

the explosion. The stoichiometric mixture containing 22.5% of nitroben-

zene gives a greater fugacity than does nitroglycerin. Pure tetranitro-

TABLE 156

Explosive Properties of Hydrocarbon-
Tetranitromethane Mixtures [18]

1 Состав смеси, %		2 Характер взрыва и действие на плиту
3 углеводород	4 тетранит-рометан	
80	20	5 Плита не изменилась
70	30	6 Плита слабо повреждена
60	40	7 Емкость углубления 25 см³
50	50	. . 125 .
40	60	8 Плита пробита
30	70	9 . сломана
20	80	10 Плита разрушена, взрыв максимальной силы
18	82	11 Плита разрушена
10	90	. .
8	92	. .
5	95	
3	97	12 Плита треснула
2	98	13 Емкость углубления 100 см³
1	99	. . 80 .
0,5	99,5	. . 40 .

1) Mixture composition, %; 2) nature
of explosion and effect on plate; 3)
hydrocarbon; 4) tetranitromethane;
5) no change in plate; 6) slight dam-
age to plate; 7) volume of depres-
sion 25 cm³; 8) plate pierced; 9)
plate broken; 10) plate destroyed,
maximum explosive force; 11) plate
destroyed; 12) plate fractured; 13)
volume of depression 100 cm³.
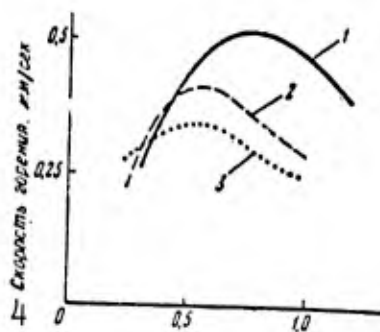
Fig. 206. Combustion rate of
mixtures of tetranitromethane
with hydrocarbon as a function
of ratio to stoichiometric com-
position. 1) Cyclohexane; 2)
isooctane; 3) n-heptane; 4)
combustion rate, mm/sec.
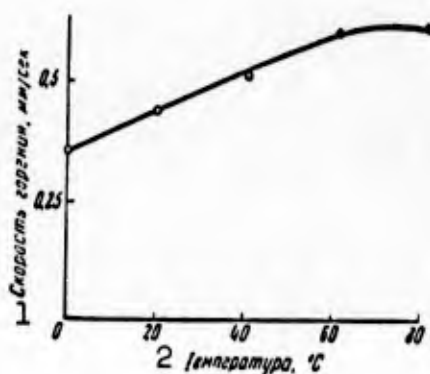
Fig. 207. Effect of temperature
upon combustion rate of mixture
of tetranitromethane with tol-
uene (0.85 of stoichiometric
composition). 1) Combustion
rate, mm/sec; 2) temperature,
°C.
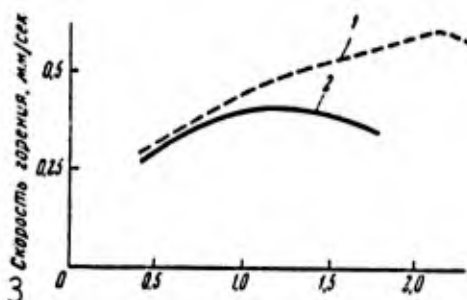
Fig. 208. Effect of ratio to
stoichiometric composition upon
combustion rate of mixtures of
tetranitromethane with benzal-
dehyde and nitrobenzene. 1)
Benzaldehyde; 2) nitrobenzene;
3) combustion rate, mm/sec.

methane and a 20% solution of it in nitrobenzene will not detonate.

The detonation rate is determined by the Dotrish method in steel

tubes having inside diameters of 21 mm on a 300-mm long section, trig-

gered by 10 g of pentrite.

The maximum detonation rate corresponds to the stoichiometric com-

position.

In 1950, an investigation was made of the explosive properties of

tetranitromethane and its mixtures with oxides of nitrogen and hydro-

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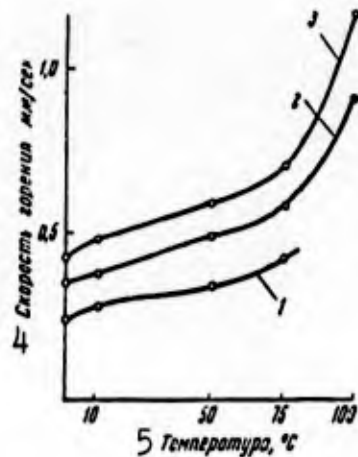
Fig. 209. Effect of temperature
upon combustion rate of mix-
tures of tetranitromethane with
benzaldehyde, for various
stoichiometric compositions.
Ratio to stoichiometric compo-
sition: 1) 1.5; 2) 1.57; 3)
2.08. 4) Combustion rate, mm/sec;
5) temperature, $^{\circ}$C.

carbons upon explosion by means of cartridges of various powers in a

lead bomb. The results of the lead-bomb channel-expansion test are

shown in Table 155.

The liability to explosion of tetranitromethane is to a large de-

gree dependent upon its purity, since very small amounts of organic

impurities increase the susceptibility to detonation. According to the

data of Rot, pure tetranitromethane (melting point, 13.8-14.1°), has

no tendency to detonate under the action of a detonator with a 10-g

tetryl grain.

The explosive properties of tetranitromethane mixed with hydrocar-

bons were investigated by means of the installation shown in Fig. 203.

The mixture under investigation, weighing 10 g, is placed in a

steel cylinder 26.75 mm in diameter, 50 mm high, and with walls 4 mm

thick. The beaker is mounted on a steel plate whose deformation (mag-

nitude of the depression) following the explosion is indicative of the

force of the explosion.

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The test results are shown in Table 156.

It is clear from the data of Table 156 that a mixture containing less than 25% of tetranitromethane mixed with hydrocarbons is safe.

Figure 204 shows the way in which explosive properties depend upon mixture composition in accordance with the depression obtained in the plate.

Stoichiometric mixtures of tetranitromethane with organic combustibles are close in sensitivity to such a highly sensitive explosive as nitroglycerin. Thus, monopropellants in this form can scarcely find application.

Berens [18] has investigated the combustion rate of liquid monopropellants taking the form of mixtures of tetranitromethane with certain combustibles: alcohols, aldehydes, and hydrocarbons. These mixtures are placed in glass tubes 5.5 mm in diameter, open at one end. The propellant is ignited, and the combustion rate determined at atmospheric pressure as a function of the stoichiometric composition and temperature. For each mixture, there is a stoichiometric composition for which the combustion rate is maximal.

Figure 205 shows the combustion rate of mixtures of tetranitromethane with several alcohols: propanol, butanol, hexanol, and octanol. Figures 206 and 207 shows the combustion rate of mixtures of tetranitromethane with hydrocarbons: toluene, xylol, cyclohexane, isooctane, and n-heptane, and Fig. 208, the combustion rate of mixtures of nitromethane with benzaldehyde and nitrobenzene.

Figure 209 shows the effect of temperature upon the combustion rate of a mixture of benzaldehyde with tetranitromethane for different stoichiometric mixture compositions. The combustion rate may double upon variation in the temperature range from 10 to 100°.

It has been suggested that a monopropellant may be made from the

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three-component mixture consisting of tetranitromethane, nitrous oxide, and ammonia: $C(NO_2)_4 + N_2O + NH_3$ [4, 11]. The characteristics of this propellant are not given in detail.

5. Propellants Based upon Hydrogen Peroxide

Hydrogen peroxide decomposes easily into oxygen and water with the evolution of a considerable amount of heat:

$$H_2O_2 \text{ (liquid)} \rightarrow H_2O \text{ (gas)} + 1/2O_2 + 12.59 \text{ kcal.}$$
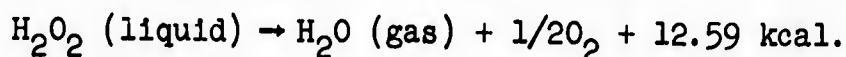
This makes it possible to utilize hydrogen peroxide as an independent low-heating-value monopropellant, characterized by a low combustion temperature.

80-90% hydrogen peroxide has found practical application as a monopropellant. It has been used in the "V-2" rocket as an auxiliary fuel for the formation of the vapor-gas mixture used to run the turbines of the pumps supplying propellant to the rocket motor. Decomposition of hydrogen peroxide is brought about with the aid of solid or liquid catalysts.

99-100% hydrogen peroxide is an insensitive explosive of the ammonium nitrate type, but it is sensitive to catalysts. 99.6% hydrogen peroxide cannot be exploded by a standard detonator cartridge in open charges. When set off in a lead bomb with a sand plug, however, an expansion of the bomb inside channel of up to 75-80 cm^3 is obtained, i.e., the same as for gunpowder.

When an additional detonator consisting of 50 g of pressed pentaerythrite is used to set off 99-100% hydrogen peroxide in 250-mm long steel tubes 34 mm in diameter with a wall thickness of 3 mm, complete detonation of the hydrogen peroxide occurs. 94% hydrogen peroxide also detonates under these conditions. The detonation does not propagate throughout the entire length of the tube in 92% hydrogen peroxide, however, but only to a distance of 100 mm from the detonator.

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90% hydrogen peroxide will not detonate under the action of an intermediate detonator or bullets fired through it. According to other data, hydrogen peroxide, in concentrations above 87%, may explode as a result of rifle fire, although this is improbable.

Certain investigators [4] maintain that mixtures that cannot be detonated from detonator cartridges in tubes may be considered safe for practical conditions. It is possible to agree with this opinion, only from the point of view of storage and transportation of the mixtures, but certainly not where they are operating in a motor.

Many organic hydrogen-containing and nitrogen-containing substances will dissolve in concentrated hydrogen peroxide without chemical interaction (methyl, ethyl, and propyl alcohols, ethyleneglycol, glycerine, acetone, acetic acid and acetic anhydride, methylmethacrylate, aniline, quinoline). Many solutions having very nearly the stoichiometric composition of complete combustion, are extremely explosive and detonate even if the container with the substance is dropped. The explosion may be comparable in force with the explosion of the corresponding amount of nitroglycerin.

Investigations have established that 90% hydrogen peroxide detonates in lead tubes under the effect of a detonator cartridge when several percent of organic substances are added; the detonation also occurs in cases in which 90% hydrogen peroxide occupies more than 30% of the volume of the mixture.

Detailed investigations have been made of the explosive properties of ternary mixtures of hydrogen peroxide and water with ethyl alcohol, acetone, and glycerine upon the basis of which triangle diagrams have been drawn in which the limits of explosive mixtures have been drawn as a function of the content of hydrogen peroxide, organic substance, and water [19].
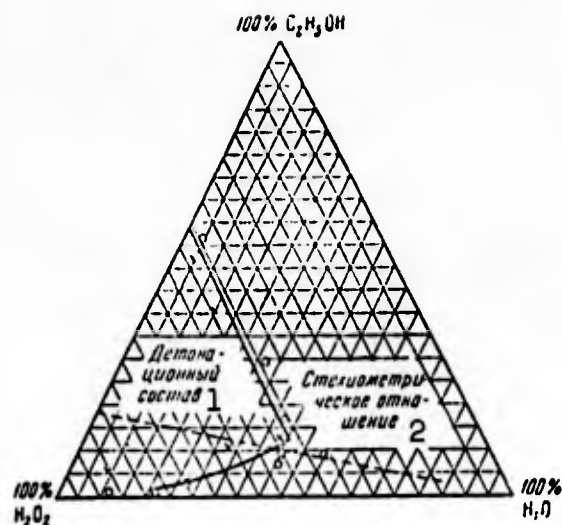
Fig. 210. Diagram for explosive
limits of mixture of hydrogen perox-
ide with ethyl alcohol and water.
x) Explosion; 0) no explosion; 1)
detonation composition; 2) stoichio-
metric ratio.
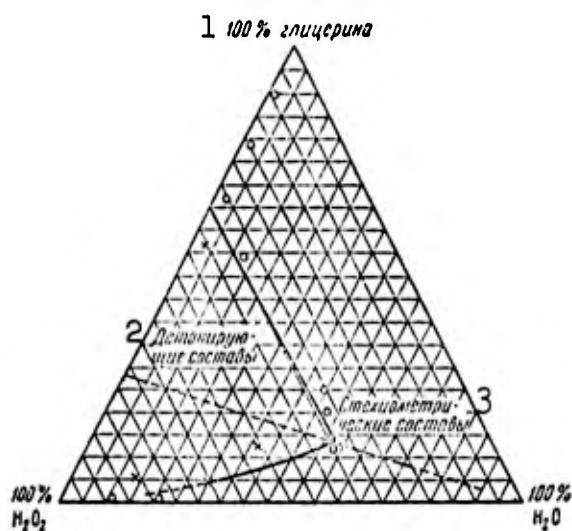
Fig. 211. Diagram of explosive
limits for mixture of hydrogen per-
oxide with glycerine and water. x)
Explosion; 0) no explosion; 1) 100%
glycerine; 2) detonating composi-
tions; 3) stoichiometric composi-
tions.

The experiments were carried out as follows: the hydrogen perox-

ide was mixed with the combustible in the required amounts behind a

panel which prevented possible harmful consequences from the explosion.

A glass tube measuring 15 x 150 (mm) with 10 ml of the mixture obtained

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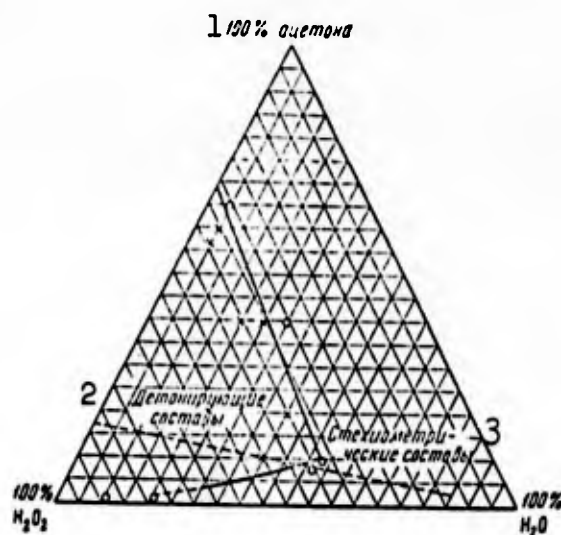
Fig. 212. Diagram of explosive
limits for mixture of hydrogen per-
oxide with acetone and water. x)
Explodes; 0) does not explode; 1)
100% acetone; 2) detonating compo-
sitions; 3) stoichiometric composi-
tions.

was placed in a lead tube 18 mm in diameter with walls 6 mm thick which
was mounted vertically on a steel plate. The propellant was exploded
by means of a detonator cartridge half immersed in the propellant. The
effect of the explosion was estimated in terms of damage to the tube.
If water alone was used in place of the propellant, the lead tube was
only bulged upon explosion of the detonator cartridge. If the lead
tube was blown into separate pieces, it was assumed that a detonation
had occurred. This method is quite rigorous. Thus mixtures that do not
detonate in these experiments may be considered [10, 19] as not being
liable to detonation under practical conditions.

Figures 210-212 show triangle diagrams for the explosive limits
of mixtures based upon hydrogen peroxide, ethyl alcohol, glycerine,
and acetone. 90% hydrogen peroxide with several percent of dissolved
combustibles added produces an easily detonating propellant [20].

The shock sensitivity of a mixture of stoichiometric composition
of 90% hydrogen peroxide with glycerine

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$$C_3H_6O_3 + 7H_2O_2 \rightarrow 2CO_2 + 11H_2O,$$
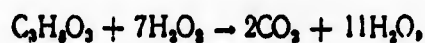
is estimated as a work of 15 kgf-m. This furnishes us a basis for classifying this mixture as a class one explosive with respect to sensitivity, of the mercury-fulminate type.

It has also been suggested that a solution of hydroxyquinoline in concentrated hydrogen peroxide be employed as a monopropellant [11].

6. Monopropellant Based upon Ethylene Oxide

Recently, it has been proposed to employ ethylene oxide [21, 22] as a liquid monopropellant.

Ethylene oxide is a gas condensing to a liquid at a temperature of $+13.5^\circ$ and freezing at -111.5°. Its density is $\rho_4^7 = 0.887$. The heat of formation of liquid ethylene oxide is $+18.29$ kcal/mole, and of gaseous ethylene oxide, $+12.19$ kcal/mole.

TABLE 157

Pressure, Decomposition-Product Composition, and Specific Thrust of Monopropellant Based upon C_2H_4O [21, 22]

1 Давление в камере двигателя, am	2 Состав продуктов в молях				Температура, °C 3	Удельный импульс, сек 4
	CO	CH₄	H₂	C₂H₄		
20	1,00	0,84	0,16	0,08	1015	159,4
30	1,00	0,86	0,14	0,07	1027	168,0
40	1,00	0,87	0,12	0,06	1033	173,6
60	1,00	0,88	0,12	0,06	1039	180,7

1) Pressure in chamber of motor, atm; 2) product composition in moles; 3) temperature, °C; 4) specific impulse, sec.

The following formula may be written theoretically for the decomposition of ethylene oxide:

$$CH_2 - CH_2 \rightarrow CO + CH_4 + 32 \text{ kcal/mole.}$$
$$\diagdown \diagup$$
$$O$$
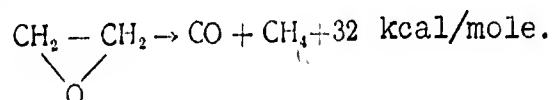
In this case, a considerable amount of heat should be developed (726 kcal/kg). In practice, however, decomposition of ethylene oxide

proceeds in accordance with the equation

$$C_2H_4O \rightarrow a\,CO + b\,CH_4 + c\,C_2H_4 + d\,H_2$$

and is associated with the formation of C_2H_4 and H_2 as side products, which decreases the heat evolution. Consequently, the heating yield of ethylene oxide is at the powder level. The temperature of the process is 1157°, and the specific impulse in a motor for a pressure ratio of 20.4:1 is 166.3 sec.

Table 157 shows the composition of products, process temperature, and specific thrust of a motor using C_2H_4O as a monopropellant, as functions of the chamber pressure.

As a monopropellant, ethylene oxide has undergone bench tests in which problems of reliability and stability of motor operation with this propellant were studied.

It is clear that ethylene oxide is relatively safe in operation, and deserves attention as a new type of monopropellant.

7. The Possibility of Obtaining Monopropellants Based upon Endothermal Compounds

Compounds that form with the absorption of heat, i.e., endothermal substances may yield heat upon breaking down into elements. The reverse process, however, that is, the decomposition of the substance into elements is not always possible in the form of a selfpropagating reaction. This depends upon the strength of the bonds, the activation energy needed to initiate the process, and several other factors. In many cases, synthesis processes leading to new compounds may occur upon decomposition of endothermal compounds, increasing the heat yield.

Table 158 shows compounds that form with the absorption of heat. The first of these compounds — hydrazoic acid — has a high heating value, but is an extremely sensitive explosive, and thus cannot be used in the pure form.

TABLE 158

Characteristics of Endothermic Compounds under Consideration as Monopropellants

1 Соединение	2 Возможные уравнения распада	3 Тепловой эффект реакции, ккал/моль	4 Теплопроизводительность, ккал/моль
5 Азотноводородная кислота	$HN_3 \rightarrow \frac{1}{2}H_2 + 1\frac{1}{2}N_2$	+67,0	1392
	$N_2 + 2H_2$	+12,05	375
6 Гидразин	$N_2H_4 <$		
	$NH_3 + \frac{1}{2}H_2 + \frac{1}{2}N_2$	+23	825
	$N_2 + 2C + 3H_2$	+12	200
7 Диметилгидразин .	$(CH_3)_2 N - NH_2 <$		
	$N_2 + 1\frac{1}{2}CH_4 + \frac{1}{2}C$		650
8 Окись азота . . .	$NO \rightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2$	−21,6	720
	$2C + H_2$	+54,19	2080
9 Ацетилен	$C_2H_2 <$		
	$\frac{1}{2}CH_4 + 1\frac{1}{2}C$	+68,1	2620
	$2C + 2H_2$	+12,5	480
10 Этилен	$C_2H_4 <$		
	$CH_4 + C$	+30,5	1130
11 Бензол	$C_6H_6 \rightarrow 6C + 3H_2$	+11,1	140

1) Compound; 2) possible decomposition equation; 3) heat yield of reaction, kcal/kg; 4) heating value, kcal/mole; 5) hydrazoic acid; 6) hydrazine; 7) dimethylhydrazine; 8) nitric acid; 9) acetylene; 10) ethylene; 11) benzene.

Hydrazine may break down according to two equations but in view of the fact that at temperatures exceeding $800°$ ammonia breaks down completely into hydrogen and nitrogen, the decomposition to nitrogen and hydrogen occurs. Here the specific impulse will amount to about 130 sec where $p/p_0 = 25$, and the process temperature is $867°K$, while if the ammonia did not decompose, it would be possible to obtain an impulse of the order of 170 sec [23, 24].

In the absence of oxygen and decomposition catalysts, liquid hydrazine is evidently a substance presenting no hazard of explosion, since hydrazine cannot be detonated by normal means.

The use of nitric oxide, acetylene, and ethylene is complicated by the fact that they are gases, while acetylene is very explosive in the compressed or liquid form.

Benzene is an example of an endothermic compound with a low heat yield, and in practice, it is not possible to cause it to decompose spontaneously into its elements.

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Chapter 9

SOLID ROCKET PROPELLANTS

1. INTRODUCTION

The first solid fuel used for rockets was black powder. Powder rockets have been used for many centuries in pyrotechnics and in warfare as a supplement to artillery. However, the rockets of past centuries had short flight ranges and low accuracy due to the low calorific value of the black powder and the imperfection of their design.

When rifled-bore weapons made their appearance, powder rockets were universally dropped from ordinance (during the second half of the last century). The recent history of solid-fuel rocket weapons begins with the Second World War.

By the beginning of 1941, the Soviet Union had developed rocket missiles using nitroglycerine powder and mobile truck-mounted installations for launching the missiles on large scales. Beginning in the summer of 1941, these rocket installations, which came to be known as "Guards Mortars" and "Katyushas," were used successfully under field conditions. The success of the new weapon was a result of the fact that a nitroglycerine powder, which is far superior to black powder in heating value, was used as the fuel. This made it possible to increase the accuracy of the fire sharply; the missiles were launched from mobile platforms with many hundreds directed at a relatively small area occupied by the enemy. During the Second World War

powder rockets came into use in other armies (German six-tube mortars), but the "Guards Mortars" remained unsurpassed until the end of the war.

During the postwar period (1945-1950), improvement of the nitroglycerine-powder rocket missiles continued, but it was at first believed that solid-fuel rockets could have only relatively short ranges (5-50 km), while ranges of 300 to 3000 km and longer would require the exclusive use of liquid-fuel rocket engines.

The working principle of a powder rocket engine is shown in Fig. 213. The nitroglycerine powder is inserted into the engine in the form of separate grains, combustion of which develops a temperature of 2500-2700°. Stable combustion of ordinary nitroglycerine powder was possible at pressures no lower than 100 atm. Since the solid-fuel rocket engine was uncooled, it could operate no longer than 1/2 to 2 sec if rupture of the walls was to be avoided. In order to prolong the burning time of the engine, it was necessary to make the combustion-chamber walls very thick, and this increased the weight of the engine.

As the production of the powder was refined, it became possible to make relatively large single-channel grains, which were secured to the engine walls at their outer surfaces; combustion proceeded from the central channel. In this case, the combustion-chamber walls were not subject to the action of temperatures and were shielded by a layer of the fuel (Fig. 214).

In recent years, new types of mixed solid fuels have been developed; these are liquid when heated and can be poured into a combustion chamber having any dimensions. On cooling, the fuel solidifies. A channel is left in the center of the charge on pouring, and combustion begins here. Mixtures of ammonium nitrate or perchlorate with
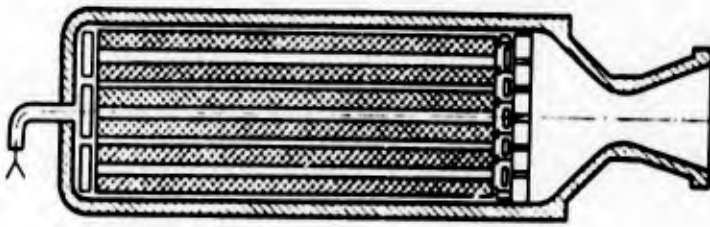
Fig. 213. Diagram of early powder rocket engine with several grains of nitroglycerine powder.
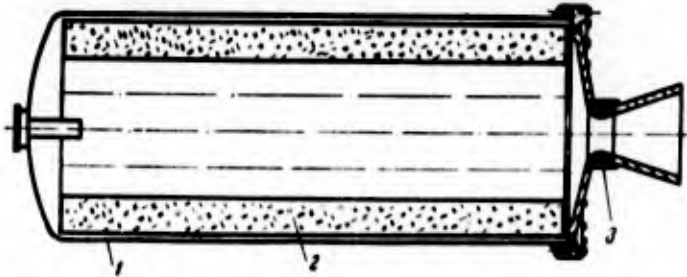
Fig. 214. Solid-fuel rocket engine with single-channel grain of cordite powder. 1) Engine casing; 2) powder grain; 3) nozzle with refractory liner.
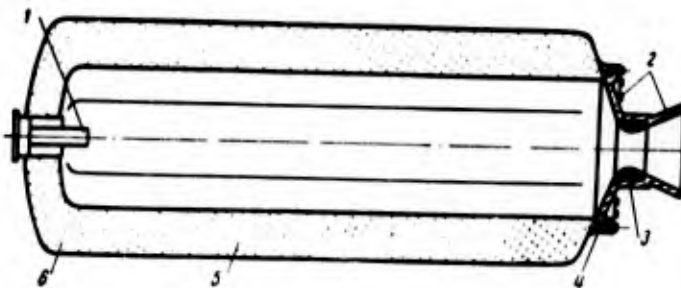
Fig. 215. Modern rocket engine with mixed solid fuel cast into combustion chamber (specific impulse 223 sec). 1) Igniter; 2) heat-resistant nozzle; 3) heat-resistant nozzle liner; 4) joint between chamber and nozzle unit; 5) cast charge; 6) combustion-chamber shell.

rubber or resins can be cited as examples of such fuels. Work on mixed solid fuels was begun in 1947 at the California Institute of Technology in the USA [1, 2]. Combustion of mixed solid fuels takes place at only moderately high pressures — 20-70 atm — from the central channel, and the heated products do not come into contact with the walls. As a result, it has been possible to reduce the weight of the engine

considerably, and to increase its burning time to several tens of seconds.
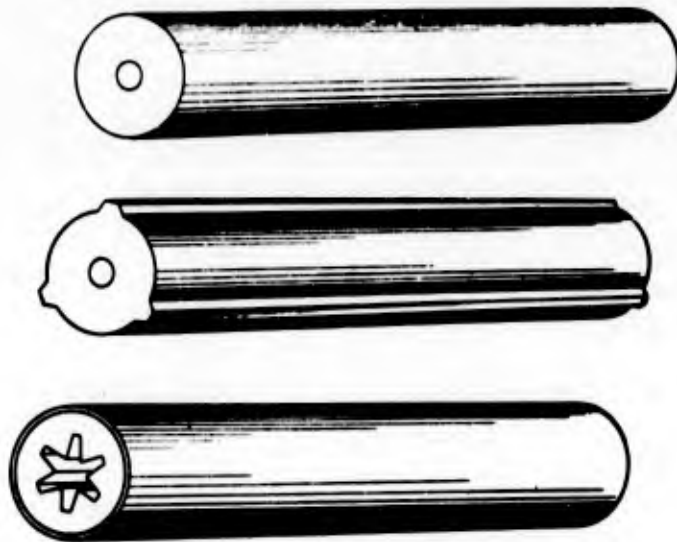
Fig. 216. Various types of mixed-solid-fuel grain charges produced by casting.
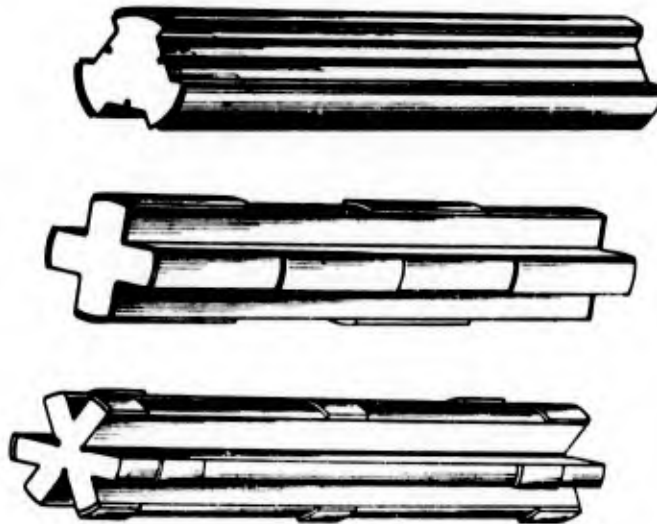
Fig. 217. Various shapes of solid-fuel charges that ensure progressive combustion rates.

The first successful tests of an engine using the mixed solid fuel in the USA were carried out in 1947, but the basic studies toward the creation of rockets were begun after 1954 [2]. In recent years, about 70% of the funds being spent on rocket fuels in the USA have gone for development of solid fuels [3, 4]; this indicates their

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increasing importance.

Figure 215 gives a schematic representation of an engine using a mixed solid fuel. The internal channel in the fuel may be smooth and cylindrical or have a more complex shape, such as a star shape (Fig. 216), and the fuel package may also have a more complex external surface (Fig. 217). In the former case, the engine develops increasing thrust as the fuel burns and the combustion surface increases. When the central channel is given a complex shape, the engine thrust may be higher during the initial phase, or, on the other hand, it may maintain a constant value during the entire combustion time, depending on the combustion surface.

The use of mixed solid fuels offers a number of advantages over the use of liquid fuels. First, solid fuels guarantee stable combustion at pressures from 20 to 70 atm, while pressures no lower than 100 atm had previously been required. Placement of the charge along the engine walls protects the engine from the effects of high temperatures until all of the fuel has burned. This makes it possible to build engines that operate for 20-60 sec, without the engine walls becoming heated above 60°.

The use of the casting method for fueling makes it possible to create large charges up to 1.5-2.5 meters and more in diameter with lengths of 5-10 meters. It was virtually impossible to produce such charges in series production by the old method of pressforming. Solid casting fuels are plastic, and can work without cracking and deforming under the combustion pressure applied from the central channel at initial temperatures of −55 to +75°.

An innovation introduced by way of improving the engines was the creation of heat-resistant insert nozzles that are capable of withstanding high temperatures (2500-2700°) without cooling for 20-50 sec,

as is the development of methods of regulating engine thrust and "cutting it off" at the proper moment – a control not previously applied to solid-fuel engines.

From the operational standpoint, solid-fuel rockets do not require fueling before launching, in contrast to liquid-fuel rockets, and are always ready for use. Starting solid-fuel engines, particularly under conditions of low pressure and weightlessness, is more dependable than that of liquid-fuel engines. Launching of solid-fuel rockets from naval vessels and submarines is less dangerous then that of rockets serviced with liquid propellants (nitric acid, liquid oxygen, etc.).

The efficiency of mixed solid fuels with specific impulses of 220-240 sec and densities of about 1.7 closely approach those of liquid rocket propellants.

The combustion chambers of solid-propellant rocket engines are made from lightweight aluminum alloys or strong reinforced plastics. Glass-filled plastics combining nylon, epoxy, and other resins with tempered glass fiber are used for this purpose. When the engine is made of a glass-filled plastic, a glass-fiber bag is woven to the shape of the chamber and impregnated with resins, after which the resins are allowed to solidify. The parting strength of the walls of a glass-filled plastic chamber may run as high as 90-95 kgf/mm^2, while that for duralumin is 42-46 kg/mm^2 and the corresponding figures for mild steel are 48-57 kg/mm^2. The engine nozzles, which must withstand high temperature, are made from alloy steel, ceramics, and graphite. All of these improvements have made it possible to reduce the weight of the engine as compared with the old metallic designs by a factor of 8 to 10, i.e., to reduce it to 7-15% of the weight of the propellant.

In the present chapter, we shall consider mixed fuels based on solid oxidants, resins, and rubbers, which give a whole series of operational advantages and a fueling technique more convenient than that for ordinary powders, the latter making it possible to design rockets of all classes [3, 4].

* * *

Let us devote brief consideration to the range of application of solid fuels in contemporary rocket engines [5-8].

Solid fuels are used in aircraft booster engines developing 400-600 and 1500-2000 kg of thrust and used in assisting takeoff, and in rocket boosters for launching liquid-propellant rockets. (Rocket boosters developing 20, 40, and 65 tons have been reported.) Another field of application of solid fuels is in rockets designed for 100-300-km ranges. An example of such a rocket is the US Army "Sergeant" rocket, which has a range of 320 km. The engine of this rocket has a total weight of 3720 kg and contains 3190 kg of propellant, i.e., 86% of the total weight. The plastic shell of the engine weighs 348.3 kg, the nozzle weighs 133.7 kg and its fire-resistant liner 40.4 kg; the weight of the explosive charge is about 100 kg. The engine operates for 23.8 sec, developing a thrust of 22,600 kg at a specific impulse of 191 sec.

The USA has developed a two-stage medium-range "Polaris" rocket with a 2400-km range. This solid-fuel rocket weighs 12.7 tons; the first-stage engine develops a thrust of 41 tons; the engine contains 9 tons of solid propellant based on ammonium perchlorate and poly-urethane resin; the specific impulse of the propellant is 240 sec. The engine diameter is 1.2 meters and its length is from 7.5 to 9 meters. The rocket's warhead weighs 450 kg. The cost of a single "Polaris" rocket is estimated at 50 million dollars. It appears that

in the not-too-distant future, most rockets with ranges below 2000 km will use solid fuels [4].

A "Super Polaris" rocket with a range of 4000 km is under development in the USA; production is set for 1964. A design has been worked out and experimental models of individual stages have been built for a "Minuteman" solid-fuel intercontinental ballistic missile. The launching weight of this rocket will be about 50 tons and its range 10,000 kilometers. A range of 6000 kilometers was attained in the first tests in 1961 [3].

The American firm "Thiokol" has developed solid fuels for a 75-ton-thrust engine; a French firm has developed a solid-propellant engine whose 60 tons of thrust are controllable [4].

Plans are being worked out for a 400-900-ton-thrust solid-propellant engine to power space rockets. An engine developing a thrust of 900 tons is being designed by the firm "North American," and will hold 360 tons of solid propellant and burn for 90 sec; at a pressure of 35 atm, the propellant will have a specific impulse of 250 sec. The engine has a diameter of 4.5 meters and a length of 20 meters [5]. In view of the difficulty of transporting such an engine, the propellant charge must be poured at the launching platform or assembled from individual blocks or segments.

At the present time, the USA is making extensive use of solid-propellant rockets for cosmic flights. Thus, the USA's first cosmic rocket, which was launched toward the Moon on 3 March 1959, was a multi-stage rocket with a launching weight of 60 tons. The first stage of this rocket was based on a "Jupiter" medium-range (2400 km) liquid-fuel missile, the second stage was a bundle of eleven solid-propellant rockets, the third stage consisted of three rockets of the same type, and the fourth stage of a single solid-propellant

rocket.

At the present time, the USA is devoting attention to hybrid engines using both solid and liquid propellants. In this case, the solid combustible is placed in the combustion chamber and the liquid oxidizer is fed from a separate tank [8a].

Between 1961 and 1969, the USA proposes to launch approximately 28-30 satellites and space rockets with some use of solid-propellant engines.

2. OXIDANTS FOR SOLID ROCKET PROPELLANTS

Various mixtures of solid oxidants (nitrates, chlorates) with combustible substances (resins, magnesium, aluminum) that burn with considerable evolution of heat and formation of gases, have been used for a long time and are known as pyrotechnic compositions. In contrast to the case of the pyrotechnic compositions, in combustion of which we attempt to achieve the maximum possible evolution of heat, accompanied by the development of high temperature and the formation of a large quantity of slag (burning compounds) or high luminosity (illuminating compounds), we require from mixed solid propellants the evolution of large quantities of gas and heat and the most complete possible conversion of this heat into mechanical work in order to produce the highest possible specific impulse from combustion of a unit weight of solid propellant. We shall examine a number of solid oxidants and the possibility of using them in solid propellants (Table 159). In practice, ammonium perchlorate, ammonium nitrate and, more rarely, potassium perchlorate are used as oxidants in mixed solid rocket propellants. Potassium nitrate is a component of black powder and is virtually never used in modern mixed powders.

Such oxidants as potassium bichromate and potassium permanganate contain too little oxygen to be used alone. They are used as combustion

TABLE 159

Properties of Various Oxygen-Containing Oxidants [9-11]

1) Химическое название	2) Формула	3) Молекулярный вес	4) Плотность при 20° C	5) Теплота образования, ккал/моль	6) Температура плавления, °C	7) Теплота об. разования, ккал/г-атом кислорода	8) Содержание кислорода, %	9) Растворимость в 100 вес. частях воды при 0°	10) Относительн. влажность насыщенного раствора соли при 20°, %	11) Теплотворн. водитель. ккал/кг*
12) Перхлораты и хлораты**										
13) Перхлорат аммония	NH₄ClO₄	117,5	1,95	+69,34	13а)(разл.)	+17,4	54,4	10,9	93	1290)
14) Перхлорат калия	KClO₄	138,55	2,324	+101,9	610	+25,4	46,3	0,76	98	805
15) Перхлорат натрия	NaClO₄	122,45	1,46	+90,68	482	+22,8	52,3	65	—	—
16) Перхлорат лития	LiClO₄	106,4	2,63	+89,98	236	+26,5	60,3	42	94,3	1300)
17) Хлорат калия	KClO₃	122,36	2,32	+95,9	368	—	39,2	3,3	—	—
18) Нитраты										
19) Нитрат аммония	NH₄NO₃	80,0	1,66	+87,1	19а)(разл.)	-21,8	60	54,2	67	555
20) Нитрат калия	KNO₃	101,1	1,30	+119,1	336	-39,9	47,5	11,6	92,5	430
21) Нитрат натрия	NaNO₃	85,0	1,38	+111,2	308	-37,0	36,3	42,2	77,2	—
22) Динитрат гидразина	N₂H₄·2HNO₃	138	—	+103,4 23)(раст.)	104	+16,5	60,3	—	—	—
24) Перекиси, перманганаты, хроматы										
25) Перекись бария	BaO₂	169,36	4,95	+132,4	450	+152,4	19	—	—	—
26) Перманганат калия	KMnO₄	158,0	2,70	+194,8	240	—	20,2	2,70	191	—
27) Бихромат калия	K₂Cr₂O₇	294,2	2,61	+488,5	398	—	20,2	4,68	—	—

*Heating value of stoichiometric mixture with polyethylene. **Nitrosyl perchlorate $NOClO_4$ [11a] and nitronium perchlorate NO_2ClO_4 [11b], which are mixed anhydrides of nitrous, nitric and perchloric acids, have been suggested for use as solid-propellant oxidants. These are solid, highly hygroscopic substances that undergo hydrolysis with formation of the free acids. They initiate combustion of many organic substances on slight heating [11c].

1) Chemical name; 2) formula; 3) molecular weight; 4) density at 20°C; 5) heat of formation, kcal/mole; 6) melting point, °C; 7) heat of formation, kcal/gram-atom of oxygen; 8) oxygen content, %; 9) solubility in 100 parts by weight of water at 0°; 10) relative moisture content of saturated solution of salt at 20°, %; 11) heating value, kcal/kg*; 12) perchlorates and chlorates:** 13) ammonium perchlorate; 13a) decomposes; 14) potassium perchlorate; 15) sodium perchlorate; 16) lithium perchlorate; 17) potassium chlorate; 18) nitrates; 19) ammonium nitrate; 19a) decomposes; 20) potassium nitrate; 21) sodium nitrate; 22) hydrazine dinitrate; 23) solution; 24) peroxides, permanganates, chromates; ... [key to Table cont'd next page]

25) barium peroxide; 26) potassium permanganate; 27) potassium bichromate.

catalysts. The effectiveness of an oxidant is determined by the amount of oxygen not bound with hydrogen or metals, i.e., by the amount of oxygen that has not lost its ability to participate in oxidation reactions with organic substances.

The largest quantities of oxygen are found in lithium perchlorate (60%) and in ammonium perchlorate (–54.5%). Ammonium nitrate contains 60% of oxygen, but only 50% is active in oxidation reactions. Oxidants containing less than 45% of active oxygen are not used in solid propellants.

Another important factor in evaluating an oxidizer is its heat of formation. This heat is positive for all of the oxidizers under consideration, i.e., the oxidant absorbs a considerable quantity of energy on its decomposition to oxygen, and this, in turn, reduces the heat effect of the reaction. Thus, the heating value of a fuel composed of ammonium nitrate and polyethylene is 915 kcal/kg; the heat of formation of the oxidant is 87.1 kcal/mole. If the heat of formation of the oxidant were zero, the heating value of such a fuel would reach 1970 kcal/kg. Consequently, it is always desirable to have oxidizers with the lowest possible heats of formation coupled with a high oxygen content.

Together with heating value, a favorable composition of the combustion products is of great importance. Thus, combustion of propellants based on potassium perchlorate results in formation of potassium chloride, which is in the gaseous state (the boiling point of KCl is 1415°) at the combustion temperature (2500°). Vaporization of a mole of potassium chloride requires 45.25 kcal. The heating value of a compound composed of potassium perchlorate and resins is 1040 kcal/kg;

if part of the energy were not expended on vaporization of the KCl, it would be 1330 kcal/kg, i.e., 300 kcal higher.

The efficiency of conversion of heat energy into mechanical work during outflow of the combustion products from the engine nozzle decreases as the composition of the combustion products becomes more complex. With $p/p_0 = 50$, this value, which is known as the thermal efficiency (η_t), diminishes as we pass from biatomic combustion products $(\eta_t = 0.582$ for H_2, N_2, CO, HCl) to triatomic products $(\eta_t = 0.446$ for CO_2, H_2O, $K_2O)$ and pentatomic products $(\eta_t = 0.248$ for B_2O_3, $Al_2O_3)$. The composition of the combustion products depends on the oxidants and combustibles used. The inflammability of the composition and the stability of its combustion, which depend to a major degree on the properties of the oxidant, are of great importance in connection with application. It is sometimes necessary to add catalysts to raise the intensity of combustion in solid propellants. A number of oxidants — particularly ammonium nitrate — decompose at a considerably higher rate and at lower temperatures in the presence of catalytic additives than they do without catalysts.

Chlorides, nitrates, and sulfates of alkali and alkaline-earth metals and basic, amphoteric, and acid oxides are used as additives to ammonium nitrate. The variation of the rate of thermal decomposition of the nitrate with the above additives has been studied in the range from 170 to $300°$, i.e., at temperatures higher than the melting point of the anhydrous nitrate $(169.6°)$. It has been noted that chromium, manganese, and copper compounds exert the strongest accelerating influence on thermal decomposition of the nitrate.

The above-described effect of catalytic additives may be accounted for by their ready decomposition with considerable evolution of heat, by virtue of which they initiate the process of decomposition

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of the oxidant [10].

The decomposition reactions of the initiating additives are:

$$(NH_4)_2Cr_2O_7 \rightarrow 4H_2O + N_2 + Cr_2O_3 + 80 \text{ kcal}$$
$$NH_4ClO_3 \rightarrow 2H_2O + \tfrac{1}{2}N_2 + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}O_2 + 100 \text{ kcal}$$
$$2NH_4NO_3 \rightarrow 4H_2O + 2N_2 + 108 \text{ kcal}$$
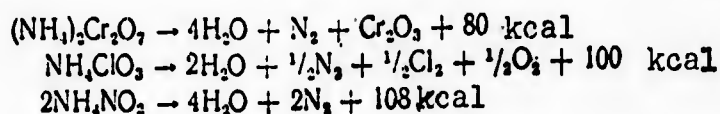
The decomposition reactions of ammonium nitrate are:

$$NH_4NO_3 \rightarrow 2H_2O + N_2O + 18 \text{ kcal}$$
$$2NH_4NO_3 \rightarrow 4H_2O + N_2 + 2NO + 14 \text{ kcal}$$
$$2NH_4NO_3 \rightarrow 4H_2O + 1.5N_2 + NO_3 + 49 \text{ kcal}$$
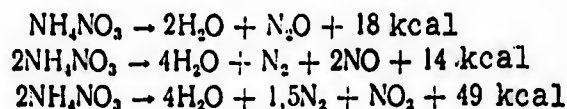
The addition of 2% of chromium trioxide, potassium bichromate, or ammonium bichromate to the fused nitrate at $200°$ results in almost instantaneous complete thermal decomposition of the entire melt. The decomposition of the nitrate melt is accelerated considerably by an additive of $CuCl_2 \cdot 2H_2O$. Such additives as $KClO_3$, $KBrO_3$, KIO_3, and $NaNO_2$ have less energetic effects. When KIO_3 is added to the melt, the latter assumes a violet coloration almost immediately and then begins to evolve iodine vapor vigorously.

On the other hand, according to literature data, addition of chlorides to the nitrate melt accelerates the decomposition process by no more than a factor of 2-3.

The accelerating effect of metallic chlorides on the thermal-decomposition process of the fused nitrate can be accounted for from a purely chemical viewpoint. In fact, as we know, the combined presence of Cl^- and NO_3^- ions results in many cases in the reaction

$$3Cl^- + NO_3^- \rightleftarrows NOCl + Cl_2 + 2O^{2-}.$$

The highly reactive nitrosyl chloride initiates the decomposition of the nitrate. Experimental data on the acceleration of nitrate decomposition by chromium compounds provide an interesting comparison with the ability of the nitrate to undergo stable combustion, as de-

scribed in the literature. At room temperature and atmospheric pressure, ammonium nitrate does not burn in pure form, but combustion starts easily when 5-10% of compounds of hexavalent chromium are added to it. Combustion of the nitrate with these additives is always preceded by heating and melting of the underlying layers, in which the above-described processes of thermal decomposition will naturally then take place.

The hygroscopicity of the oxidant, i.e., its ability to absorb moisture from the air and become moist, a property related to the solubility of the salt in water, is of great importance under operational conditions. In practice, work with salts is difficult when the relative moisture content above their saturated solutions is below 80%. The rate of absorption and the quantity of moisture absorbed from the air by a given salt depends not only on the chemical nature of the salt and the temperature and relative humidity of the air, but also on the surface of the salt and the strength of its film of the resin used in the propellant.

Apart from the general properties of the oxidants and their effectiveness, their natural reserves and the production capacity for them are of importance. Thus, ammonium nitrate is a product many tons of which are produced by the contemporary chemical industry. The production of ammonium nitrate in the USA runs to about 2 million tons. per year. In 1959, the USA's production capacity for ammonium perchlorate was 100,000 tons per year, and the output during this same year was 10,000 tons [10]. In 1955, lithium perchlorate production in the USA was only one ton [10].

Apart from oxygen compounds, fluorine compounds can also act as oxidants. Compounds of fluorine with sufficiently high fluorine contents and low heats of formation — gases or liquids — may be regarded

TABLE 160

Inorganic Fluorides with High Fluorine Contents [12, 13]

1) Химическое название	2) Формула	3) Теплота образования, ккал/моль
4) Тетрафторид титана	TiF_4	—
5) Тетрафторид олова	SnF_4	—
6) Трифторид хрома	CrF_3	286
7) Гексафторид сурьмы	SbF_6	—
8) Пентафторид вольфрама . . .	WF_5	—
9) Гексафторид молибдена . .	MoF_6	300
10) Декафторид серы	S_2F_{10}	480
11) Калий марганец гексафто-рид	$KMnF_6$	—
—	$BrSbF_6$	—
12) ...лий бром тетрафторид . .	$KBrF_4$	—

1) Chemical name; 2) formula; 3) heat of
formation, kcal/mole; 4) titanium tetra-
fluoride; 5) stannic tetrafluoride; 6)
chromium trifluoride; 7) antimony hexa-
fluoride; 8) tungsten pentafluoride;
9) molybdenum hexafluoride; 10) sulfur
decafluoride; 11) potassium manganese
hexafluoride; 12) potassium bromotetra-
fluoride.

only as liquid-propellant components. Fluorine forms a whole series
of fluorides with metals and nonmetals. However, metal fluorides,
regardless of their high fluorine contents, have excessively high
heats of formation, so that propellant mixtures based on them are
not efficient. Among the inorganic fluorides, we may note those
listed in Table 160 as containing large quantities of fluorine.

None of the fluorides listed can be regarded as an efficient
oxidizer.

A number of organic fluorine derivatives may also be regarded
as oxidizers. In organic compounds, fluorine replaces carbon [sic]
atoms with formation of perfluoro derivatives that are known as fluoro-
carbons [14]. The fluorocarbons are oxidizers with respect to metals.
Among the solid compounds of this type, we shall consider perfluoro-

hexadecane — $C_{16}F_{34}$, m.p. 115°, b.p. 240°, $d_{20}^{4} = 1.98$, $q_{obr} = +1340$ kcal/mole.

Its reaction with boron can be represented by the equation

$$C_{16}F_{34} + 11\tfrac{1}{3}B \rightarrow 16C + 11\tfrac{1}{3}\,BF_3 + 3350 \quad \text{kcal}$$
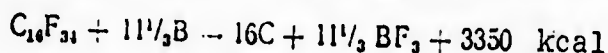
Among the fluorocarbons, however, the greatest interest is attracted by high-molecular-weight compounds that can serve as binders simultaneously. Teflon $(C_2F_4)_x$ is such a polymer; it is produced on polymerization of gaseous tetrafluoroethylene monomer, C_2F_4. Teflon is extremely resistant to attack by various reagents, including concentrated nitric acid. It has a high density, excellent mechanical properties, is heat-resistant, and undergoes no changes during long periods at 250°. Teflon bears the technical name "Fluoroplast-4" and has the following properties:

Specific gravity 2.1-2.3
Melting point .... 327°
Vitrification point .... -120°
Heat of formation of $(C_2F_4)_x$ .... $x \cdot 174$ kcal
Ultimate tensile strength .... 140-200 kgf/cm^2
Molecular weight 250,000

TABLE 161

Characterization of Propellant Mixtures of Fluorides with Boron and Magnesium [12,13,16]

1) Рассматриваемая топливная смесь	2) теплопроизводительность, ккал/кг	3) Удельный импульс $(p/p_0 = 50)$, сек.
$S_2F_{10} + B$	1670	220
$BrSbF_8 + B$	1400	180
$C_{16}F_{34} + B$	2160	150
$C_{16}F_{34} + Mg$	1740	—
$(C_2F_4)_x + B$	1850	150

1) Propellant mixture; 2) heating value, kcal/kg; 3) specific impulse $(p/p_0 = 50)$, sec.

"Fluoroplast-4" can be prepared in the form of a fine powder or in the form of films; various products are manufactured from it [14].

Table 161 presents the characteristics of fuel mixtures based on fluorine derivatives of hydrocarbons and fluorides.

Thus, known solid fluorine oxidizers have no advantages over oxygen-containing oxidizers.

Completely fluorinated polyamines containing the NF_2 grouping may be of some interest among the organic fluorine derivatives.

The literature contains references [12, 16] to perfluorinated nitrogen-containing compounds such as

$$CF_2 = CF - CF - NF_2; \quad \begin{array}{c} F_3C \\ \\ F_3C \end{array} \!\!\! \Big\rangle C = CF - NF_2; \quad \begin{array}{c} F \\ \\ F \end{array} \!\!\! \Big\rangle C = N - F.$$
$$\qquad\quad \overset{|}{CF_3}$$
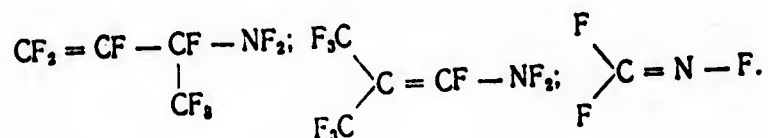
However, the content of $>NF$ and $-NF_2$ groups in them is too small to make them effective oxidants.

3. DESCRIPTION OF COMBUSTIBLES AND BINDERS FOR SOLID FUELS

Prime interest will attach to those combustibles during combustion of which the largest quantities of heat are evolved. These include beryllium, boron, magnesium, aluminum, and the hydrocarbons. The heating value, heating yield, and gas production of a number of combustibles with oxygen and ammonium perchlorate as oxidizers are listed in Table 162.

Of all the known combustibles, only seven or eight produce propellant mixtures with ammonium perchlorate having heating yields above 1000 kcal/kg. All others have lower heating yields.

As regards both heating value and heating yield, all of them are considerably inferior to propellant mixtures with hydrocarbons and for this reason are of no interest as rocket-propellant combustibles. The heating yield of fuels with magnesium and beryllium is considerably higher than that of the others listed in Table 162 as a result of the fact that magnesium and beryllium oxides do not vaporize. However, heating yield is not alone sufficient to produce high specific impulses. Thus, the theoretical impulse for the NH_4ClO_4 – Mg system (2440 kcal/kg) is lower than that for NH_4ClO_4 $-C_nH_{2n}$ (1280 kcal/kg), since in the former case the gas formation is less than half that in the latter

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case.

TABLE 162

Heating Value and Heating Yield of a Number of Combustibles with Oxygen and Ammonium Perchlorate as Oxidizers [15].

1) Горючее	2) Формула окисла	3) Теплотворная способность, ккал/кз	4) Теплопроизводительность, ккал/кз	
			5) окислитель кислород	6) окислитель перхлорат аммония
7) Водород	H_2O	28 900	3215	1570
8) Углерод	CO_2	7 840	2140	1106
9) Бериллий	BeO	16 200	5800*	3400*
10) Бор	Be_2O_3	13 956	3300	1560
11) Литий	Li_2O	10 300	3760	670
12) Алюминий	Al_2O_3	7 290	2680	1260
13) Магний	MgO	6 000	3630*	2440*
14) Кремний	SiO_2	7 160	2060	1040
15) Углеводороды . . .		10 300	2270	1280

*For all other combustibles, the heating yield is given with correction for the heat expended on vaporization of the oxides, with the exception of magnesium and beryllium, whose oxides do not vaporize.

1) Combustible; 2) formula of oxide; 3) heating value, kcal/kg; 4) heating yield, kcal/kg; 5) oxygen as oxidizer; 6) ammonium perchlorate as oxidizer; 7) hydrogen; 8) carbon; 9) beryllium; 10) boron; 11) lithium; 12) aluminum; 13) magnesium; 14) silicon; 15) hydrocarbons.
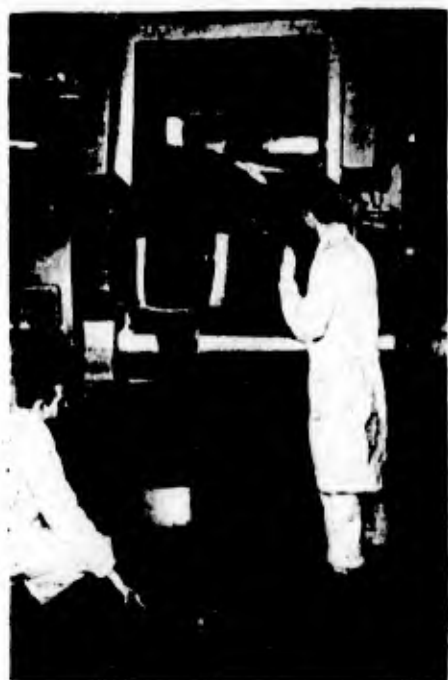
Fig. 218. Insertion of solid-propellant charge by pouring after preparation in mixer.

The basic combustibles in solid rocket propellants are organic materials in the form of high-molecular compounds — synthetic resins and rubbers — which simultaneously perform the functions of binders holding the oxidizer particles together and produce a large gaseous phase on combustion.

The following are most widely used: polyurethane resins, epoxy resins, polysulfide rubbers, natural

and synthetic rubbers, various nitro polymers, polyester resins, and nitrocellulose.

When the appropriate resins are mixed in the molten or liquid state with oxidants, the result is a doughlike mass that can be poured into the engine chamber (Fig. 218). On cooling and appropriate processing, these compounds solidify, but retain their low thermoplasticity and will not crack on sharp changes in temperature.

The USA has developed mobile units for mixing the components of solid propellants (oxidizer and polymers) and fueling the rocket on the launching pad. This installation can produce 2000-2500 kg of propellant per hour [16a].

All of the necessary physicomechanical properties can be secured in a charge by using high-molecular materials as combustibles (Table 163).

Let us consider specific types of resins and rubbers.

Polyurethane resins and rubbers. The chains of these polymers may, for example, contain the following groups:

$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-NH-(CH_2)_6-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_4-O-\overset{\overset{\displaystyle O}{\|}}{C}-NH-(CH_2)_6-NH-$$
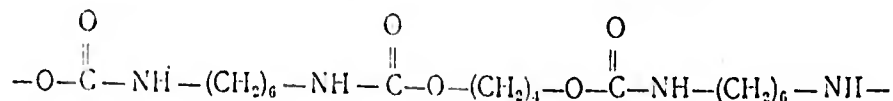
Polyurethane resins and rubbers are distinguished by high flexibility and strength; this is partly the result of the presence of $>NH$ and $O=C<$ groups, between which hydrogen bonds form: $>N-H...O=C<$; this intensifies the interaction between the polymer chains.

The initial monomers used for the preparation of polyurethanes are a diisocyanate and a dibasic alcohol (glycol) or polyesters having terminal hydroxyl groups.

The compounds most widely used to produce the polyurethanes are hexamethylenediisocyanate $O=N=C-(CH_2)_6-C=N=O$, 2,4-toluenediisocyanate $CH_3C_6H_3(NCO)_2$, butanediol-1,4 $HO-(CH_2)_4-OH$, the diethylene glycol

TABLE 163

Structure of Certain Binders for Solid Propellants [14, 17]

1) Наименование	2) Эмпирическая формула	3) Структура полимерной цепи	4) Теплотворная способность, ккал/кг
5) Натуральный каучук ..	C_5H_8	$\left[-CH_2-\underset{\underset{CH_3}{\mid}}{C}=CH-CH_2-\right]_x$	10400
6) Синтетический каучук (бутадиен + стирол) ..	—	$\left[-CH_2-CH=CH-CH_2-\underset{\underset{C_6H_5}{\mid}}{CH}-CH_2-\right]_x$	10200
7) Полисульфидный каучук	$C_4H_8OS_4$	$\left[-C_2H_4-O-C_2H_4-\underset{\underset{S}{\parallel}}{S}-\underset{\underset{S}{\parallel}}{S}-\right]_x$	5600
8) Полиуретановые каучуки	C_xH_yON	$\left[\begin{array}{l}-O-CO-NH-(CH_2)_6-NH-CO\\-O-C_2H_4-O-C_2H_4-O-C_2H_4-O\end{array}\right]_x$	7250
9) Битумы	$C_xH_yO_z$	—	—
10) Нитроцеллюлоза	$C_6H_7O_{11}N_3$	$[C_6H_7O_2(ONO_2)_3]_x$	—
11) Фенольно-формальдегидные смолы	—	$\left[-\underset{\underset{}{\overset{OH}{\mid}}}{\bigcirc}-CH_2-\right]_x$	—
12) Карбамидные смолы .. .	—	$[-NH-CO-NHCH_2-]_x$	—
13) Полиакриловые смолы ..	—	$\left[-CH_2-\underset{\underset{COOR}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-\right]_x$ и $\left[-CH_2-\underset{\underset{COOCH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-\right]_x$	—
14) Полиэфирные смолы .. .	—	$\left[-OOC-\bigcirc-COOC_2H_4-\right]_x$	—

1) Name; 2) empirical formula; 3) structure of polymer chain; 4) heating value, kcal/kg; 5) natural rubber; 6) synthetic rubber (butadiene + styrene); 7) polysulfide rubber; 8) polyurethane rubbers; 9) asphalts; 10) nitrocellulose; 11) phenol-formaldahyde resins; 12) urea resins; 13) polyacrylic resins; 14) polyester resins.

ester of adipic acid $HOC_2H_4OOC(CH_2)_4COOC_2H_4OH$, and the polyglycols [17a]. All of these compounds are produced from readily available raw materials.

The resin is prepared by mixing the diol with the diisocyanate. The reaction begins at room temperature, and then the temperature is raised to $90-95^{\circ}$ and held there for a certain time, after which it is

further increased to 190-200° to bring the process to completion. During the first phases, the diisocyanate is in a viscous state and can be mixed with the oxidizer, with subsequent solidification by an excess of the diisocyanate.

The formation of polyurethane resins is an example of stepwise polymerization in which no water or other splitting product is formed. The reaction takes place as follows:

$$HO(CH_2)_xOH + O = C = N - (CH_2)_6 - N = C = O \rightarrow$$

$$\rightarrow HO - (CH_2)_x - O - \overset{\overset{O}{\|}}{C} - NH - (CH_2)_6 - NH - \overset{\overset{O}{\|}}{C} - O(CH_2)_x - O - \overset{\overset{O}{\|}}{C} - NH -$$
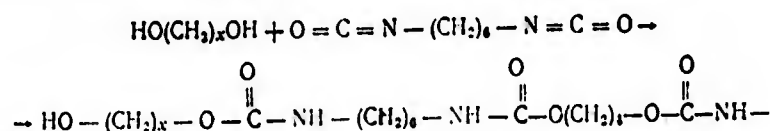
The molecular weight of the products increases with increasing temperature and reaches 10,000-15,000.

Polyurethanes possess considerable resistance to oxygen and oxidizing agents. The elastic properties of polyurethanes are retained at low temperatures; the resins possess high adhesion to various materials and particles of mineral salts that are oxidizers. Polyester urethanes retain their flexibility, and this ensures good antifrost properties in the compositions.

Epoxy resins. Epoxy resins possess high adhesion and excellent elastic properties; while originally viscous and fluid, they are capable of subsequent solidification.

The resins are produced by condensation of epichlorohydrin with bis-phenols:
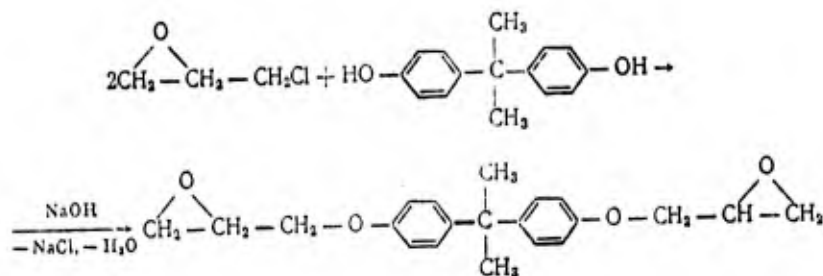
The resulting ether is again reacted with diphenylpropane, with

the resultant formation of a polymer chain having the following
structure:

$$CH_2-CH-CH_2-\left[-O-\bigcirc-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\bigcirc-O-CH_2-\overset{\overset{OH}{|}}{CH}-CH_2-\right]_n$$
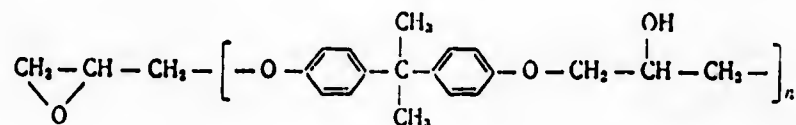
The molecular weight of the polymers runs from 1000 to 4500.
The melting point of a resin having a molecular weight of 1500-2000
is about $45-55^\circ$; in the molten state, the resin can again be mixed
with oxidizer particles.

The resins are viscous or low-viscosity brittle masses, very
sticky in molten form or in solution, with high adhesion to most
materials; they contain functional epoxy groups with which a number
of substances enter into reactions; this results in increases in their
molecular weights. Such substances are polyamines, acid anhydrides,
and others; solidification of the epoxy compositions takes place as
a result of reactions with them. The solidification reaction is con-
ducted at normal temperatures and high speed with addition of a
"solidifier." The solidified resin acquires the structure of a high-
molecular polymer with a three-dimensional network; its softening
temperature is $100-150^\circ$.

An adhesive epoxy film on the surfaces of the oxidizer particles
delivers higher binding strength than does any other resin. Epoxy
resins have specific gravities from 1.2 to 1.3, ultimate tensile
strengths of 570-700 kgf/cm^2, and thermal stability to $100-120^\circ$; they
are also used to produce glass-filled plastics that are used in the
manufacture of the rocket-engine casings; with their relatively low
density (1.7-1.8), such glass-filled plastics have tensile strengths
from 3000 to 4000 kgf/cm^2 and are superior to aluminum in this respect.

Polyester resins. Polyester resins may also be used in solid

propellants. They are produced by polycondensation reaction between dibasic acids or their anhydrides and bi- or trifunctional alcohols. The following acids or anhydrides are used:

phthalic acid

isophthalic acid

maleic anhydride
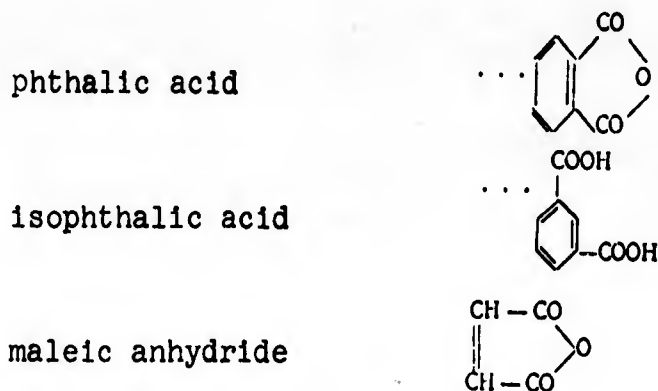
The following polybasic alcohols are used:

Ethylene glycol ....$C_2H_4(OH)_2$
Glycerine ....$C_3H_5(OH)_3$
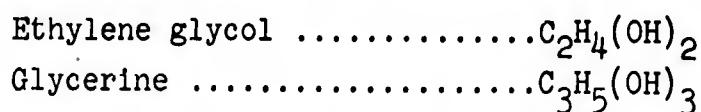
The polycondensation is based on an esterification or reesterification reaction and takes place with the mixture components heated to $150-180^\circ$ and higher. The result is formation of polyester chains:
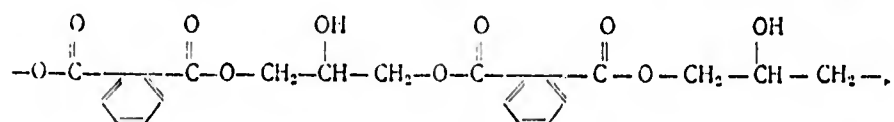
which are then "knitted together" by an excess of acid at the hydroxyl groups. Then the resin solidifies due to the formation of a three-dimensional structure. In the intermediate phase, the resin has a preferentially linear structure. Further hardening takes place on heating to $160-200^\circ$.

Maleic anhydride is used with ethylene glycol or diethylene glycol to produce unsaturated polyesters. Formation of the unsaturated polyester takes place at $170-220^\circ$. The unsaturated polyester is then co-polymerized with the appropriate monomers, such as styrene, etc. The molecular weights of the unsaturated polyesters lie in the range from

2500 to 5000.

The unsaturated polyesters are extensively used to produce glass-filled plastics from which the combustion chambers of the rocket engines are manufactured.

Rubbers. Propellants based on ammonium nitrate and various forms of rubber have been developed in the USA by the firm "Thiokol." The rubbers used are natural, synthetic, polysulfide, and polyurethane types. The widespread use of rubbers in rocket propellants is the result of their excellent physicomechanical properties and high strengths:

	Tensile strength, kgf/cm^2	Elongation, %
Natural rubber	300-320	600-700
Butadiene-styrene rubber	250-280	–
Polysulfide rubber	100-120	300-600
Polyurethane rubber	350-400	–

Polysulfide rubbers have come into extensive use as binders and combustibles in solid propellants; they are produced by polycondensation of dihalogenated alkyls with polysulfides of alkali metals. The initial materials used are as follows:

1) Дихлорэтан . . . . .ClC₂H₄Cl
2) Дихлордиэтиловый эфир . . . .ClCH₂CH₂OCH₂CH₂Cl
3) Дисульфид натрия . . . . . . .Na₂S₂
4) Тетрасульфид натрия . . . . .Na₂S₄

1) Dichloroethane; 2) dichlorodiethyl ether;
3) sodium disulfide; 4) sodium tetrasulfide.

The polycondensation reaction takes place according to the equation

$$x\mathrm{Na_2S_4} + x\mathrm{ClC_2H_4Cl} \rightarrow [-\mathrm{CH_2 - CH_2 - S} \overset{\|}{\underset{S}{}} \mathrm{S} \overset{\|}{\underset{S}{}} -]_x + 2x\mathrm{NaCl}$$
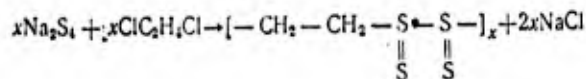
Polysulfide rubbers are known by the name "thiokols" and are subjected to vulcanization with metal oxides (zinc oxide) and oxidizing agents. All of the rubbers are used in considerable excess in the

propellant composition in order to obtain high strength. However, an excess of rubber or resin in the composition causes a sharp deterioration of the oxygen balance and lowers the heating yield.

The heating yield of the propellant varies as follows as a function of ammonium-perchlorate and resin contents:

Content of rubber or resin, %	30	25	20	15	10
Oxidizer content, %		70	75	80	85	90
Heating yield, kcal/kg			698	864	1010	1050	1260

A fuel containing 20-25% of rubber has a large combustible excess and a lowered heating value.

With the object of improving oxygen balance while retaining the necessary binding properties, the American firm Aerojet General, which is developing solid propellants, has produced binders based on nitro polymers injection of 20-25% of which maintains an oxygen balance close to zero with retention of the necessary plastic properties in the charge.

Nitrocellulose $[C_6H_7O_2(ONO_2)_3]_x$ can be used as the nitro polymer.* However, it has the disadvantage of lacking thermoplastic properties.

Nitropolyurethane has been mentioned as a binder that contains active oxygen; it is added to the oxidizer in quantities of 65 to 70% [15].

Apart from the polymers, nitro derivatives — nitrocellulose, dinitrotoluene, and trinitrotoluene, combustion of which requires smaller quantities of oxygen — are added to certain compositions. Thus, the following proportions between ammonium perchlorate and trinitrotoluene correspond to the stoichiometric composition at zero oxygen balance: NH_4ClO_4 — 58.5%; $C_6H_2(NO_2)_3CH_3$ — 31.5%.

The heating yield of such a propellant mixture attains 1260 kcal/kg, i.e., the heating yield of the stoichiometric perchlorate-rubber mix-

ture with its content of only 7-8% of rubber.

4. SOLID-PROPELLANT COMPOSITIONS

Solid rocket propellants in practical use incorporate ammonium perchlorate and ammonium nitrate as oxidizers and binding rubbers and resins as combustibles. Moreover, various additives of metals, combustion catalysts, and the like are added in many cases. Development of solid-propellant recipes has been under way in the USA for about ten years, from 1947 to 1957. The result of these studies has been the creation of commercial samples of propellants delivering specific impulses from 175 to 240 sec at a pressure drop of 40 atm. It was expected that fuels with specific impulses as high as 260 sec would be created by 1960 [1]. Certain authors are of the opinion that creation of solid propellants with specific impulses as high as 300 sec is theoretically possible [18].

Propellant recipes are developed on the basis of energy requirements and technological fueling possibilities. The latter are, in turn, determined to a major degree by the energy characteristics of the propellant, since it is necessary to introduce a large excess of binder to ensure strength and the possibility of casting the compound. To evaluate the limiting energy possibilities of a fuel, it is convenient to examine binary propellant mixtures of stoichiometric composition. A preliminary rough calculation is made from the familiar formulas, without taking dissociation of the combustion products and heat losses into account:

$$P = 9.33 \sqrt{\eta_t \cdot H} \tag{1}$$

$$P = \frac{0.863}{g} \sqrt{\eta_t \frac{k}{k-1} \frac{H \cdot V}{C_p}}, \tag{2}$$

where P is the specific impulse in sec; H is the heating yield of 1 kg of fuel in kcal; V is the specific volume of the combustion

products in liters/kg, C_p is the heat capacity of the combustion products at the temperature of the process, and η_t is the thermal efficiency of the process, which is found by the formula

$$\eta_t = 1 - \left(\frac{p_0}{p}\right)\frac{k-1}{k}$$

(p_0 is the nozzle-section pressure, $\underline{p}$ is the combustion-chamber pressure and $\underline{k}$ is the adiabatic exponent, i.e., the ratio C_p/C_v).

The thermal efficiency depends on the composition of the combustion products, since it has different values for monatonic, biatomic, and triatomic gases, as well as on the pressure drop in the chamber and at the nozzle section.

The thermal efficiency characterizes the fraction of thermal energy converted into work when the propellant burns. In cases where the combustion products are polyatomic, less favorable conditions are created for conversion of the propellant's heat energy into work.

When the composition of the combustion products is complex, the thermal efficiency is computed additively as a function of the mole fractions of the individual components:

$$\eta_t = \eta_t' \cdot x_1 + \eta_t' \cdot y + \eta_t'' \cdot z,$$

where $\underline{x}$, $\underline{y}$, and $\underline{z}$ are the mole fractions of the individual components ($x + y + z = 1$), and $\eta_t^!$, $\eta_t^"$, and $\eta_t^{!"}$ are the thermal efficiencies of components $\underline{x}$, $\underline{y}$, and $\underline{z}$.

The heat capacities of the combustion products are found by the appropriate formulas [10]:

Substance	Molar heat capacity (C_p)
O_2, N_2, HCl, CO . .	$6,5 + 0,0010\ T$
H_2O	$8,81 + 0,0019\ T$
CO_2	$7,0 + 0,0071\ T$
BeO	$16\ [2600°\ C]$
MgO	$16\ [2800—3000°C]$

The heat capacities of a number of oxides in the solid state at

- 603 -

TABLE 164

Heats of Formation of Oxides, Fluorides, and Chlorides in Solid and Gaseous States

1) Соединение	2) Температура, °C		5) Теплота образования, ккал/моль	
	3) плавления	4) кипения	6) в твердом состоянии	7) в парообразном состоянии
8) *Окислы*				
Li₂O	—	1700	142,6	43,68
BeO	2547	3900	143,0	—
MgO	2800	3600	143,8	—
B₂O₃	577	1700	305,4	214,8
SiO₂	1425	2230	210	79,17
Al₂O₃	2050	2250	402,0	222,7
CO₂	—	—	—	94,052
H₂O	—	—	—	57,798
9) *Фториды и хлориды*				
LiF	870	1670	146,3	82,7
BeF₂	—	—	241,8	186,8
MgF₂	—	—	263,5	176,5
BF₃	10) Газ	—	—	267,0
SiF₄	»	—	—	373,0
AlF₃	1040	—	355,7	281,3
CF₄	10) Газ	—	—	218(187)
HF	—	—	—	64,2
LiCl	—	—	94,3	43,8
HCl	—	—	—	21,89

1) Compound; 2) temperature, °C; 3) of melting;
4) of boiling; 5) heat of formation, kcal/mole;
6) in solid state; 7) in gaseous state; 8) oxides;
9) fluorides and chlorides; 10) gas.

$1000°$ have the following values according to handbook data [10]:

$$Al_2O_3 \ldots\ldots 0.31 \text{ kcal/g·degree}$$
$$MgO \ldots\ldots\ldots 0.32 \text{ kcal/g·degree}$$
$$SiO_2 \ldots\ldots\ldots 0.284 \text{ kcal/g·degree}$$
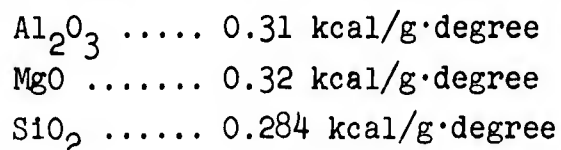
The heating yield (H) is found as the difference between the heats of formation of the reaction products and the heat of formation of the initial compounds, divided by the over-all molecular weight of the initial mixture. The heating yield is found on the basis of the condition that the reaction products be cooled to $20°$ and the water remain in the gaseous state.

If the products of combustion of solid propellants contain metal

and nonmetal oxides that are liquid or solid under ordinary conditions, the heating yield is figured taking into account the heat expended on vaporization and melting of the oxides; i.e., the heat of formation of the oxides in the gaseous state is taken for the calculation. Here it is necessary to take the most nearly correct value for the heat of formation of the oxide in the gaseous and solid states. Thus, the data given for boron anhydride indicate a heat of formation from 279 to 305 kcal/mole and a heat of sublimation from 65.6 to 77.6 kcal/mole. Depending on the value taken for the heat of formation, the specific-impulse value may vary by 15 to 20 units [19]. This scattering in the heat-of-formation values is related to the difficulty of determining these values for many oxides.

TABLE 165

Theoretical Characteristics of Propellant Mixtures with Ammonium Perchlorate, Beryllium, and Lithium for $p/p_0 = 68$, according to Blackman, 1961 [18a]

окислитель, % 1)	Связующее, % 2)	Бериллий, % 3)	Литий, % 4)	Удельный импульс, сек. 5)	Температура горения, °K 6)
70	10	20	—	280	3400
70	10	14	6	288	3450
70	10	10	10	285	3200
70	10	6	14	275	3000
70	10	—	20	266	2400

1) Oxidizer, %; 2) binder, %; 3) beryllium, %; 4) lithium, %; 5) specific impulse, sec; 6) combustion temperature, °K.

Table 164 lists values selected for the heats of formation of oxides from recent literature data.

Calculations of specific impulse without taking dissociation of the combustion products into account are inaccurate (errors of the order of ±2%), but are sufficient for preliminary evaluation of the energy properties of propellants.

The comparatively small difference between the two methods of

calculation results from the fact that although the heating yield is lowered on dissociation of the combustion products, the thermal efficiency is raised simultaneously, and this stabilizes the product $\eta_t \cdot H$ in the formula $P = 9.33\sqrt{\eta_t \cdot H}$ to a certain degree.

Let us examine the calculated characteristics of the binary propellant mixtures listed in Tables 165 and 166. As regards their efficiency, solid oxidizers used in propellant mixtures with organic combustibles (polyethylene) array themselves in the following series:

	Heating yield, kcal/kg	Specific impulse $(p/p_o = 50)$, sec
$NH_4ClO_4 + C_nH_{2n}\ldots$	1260	232
$LiClO_4 + C_nH_{2n}\ldots$	1300	234
$NH_4NO_3 + C_nH_{2n}\ldots$	955	197
$KClO_4 + C_nH_{2n}\ldots$	805	180
$KNO_3 + C_nH_{2n}\ldots$	450	120

Oxidizers of the first four compositions are of greater interest as solid-propellant oxidants.

The introduction of boron and aluminum into solid propellants will raise the specific impulse, since the specific impulse of the aluminum/ammonium perchlorate composition is somewhat higher than that of the ammonium perchlorate/resin propellant, while the specific impulse of the ammonium perchlorate/boron system is considerably higher.

Combustion of solid propellants containing metallic combustibles may proceed in either of two directions: toward formation of the metal oxide and water (1) or, when an excess of metal is present, toward formation of the metal oxide and hydrogen as a result of reduction of the metal by the water vapor (2):

$$NH_4ClO_4 + 1{,}66Al \rightarrow HCl + 1\tfrac{1}{2}H_2O + 0{,}835Al_2O_3 + \tfrac{1}{2}N_2 \qquad (1)$$
$$NH_4ClO_4 + 2{,}66Al \rightarrow 1{,}5\,H_2 + HCl + 1{,}33Al_2O_3 + \tfrac{1}{2}\,N_2. \qquad (2)$$
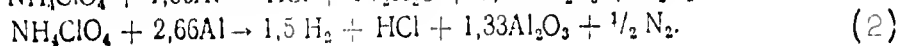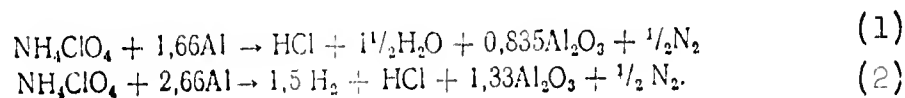
We present the characteristics of these processes:

TABLE 166

Calculated Characteristics of Solid Propellant Mixtures as Compared with Liquid Propellants for $p/p_0 = 50$

1) № п.п	2) Топливные смеси	3) Плотность	4) Теплопроизводительность, ккал/кг	5) Термический к.п.д. (η_t)	6) Удельный импульс, сек.	7) Удельное газообразование, л/кг
	8) *Твердые топливные смеси*					
1	NH_4NO_3 — 94,5% C_nH_{2n} — 5,5%	—	955	0,472	198	970
2	NH_4ClO_4 — 90,9% C_nH_{2n} — 9,1%	1,77	1260	0,486	232	810
3	NH_4ClO_4 — 68,5% $C_6H_2(NO_2)_3CH_3$ — 31,5% 9) (тринитротолуол)	—	1260	0,49	232	—
4	$KClO_4$ — 88% C_nH_{2n} — 12%	—	805	0,48	180	530
5	$LiClO_4$ — 85% C_nH_{2n} — 15%	1,92	1300	0,48	234	650
6	NH_4NO_3 — 60% Al — 40%	2,02	1070	0,52	203	—
7	NH_4ClO_4 — 61,8% Al — 38,2%	2,19	1250	0,534	242	514
8	NH_4ClO_4 — 80% B — 20%	2,06	1560	0,48	254	660
9	$LiClO_4$ — 55,6% Al — 44,4%	2,54	1560	0,40	232	—
10	NH_4ClO_4 — 78% $B_{10}H_{14}$ — 22%	1,70	1530	0,51	260	—
11	NH_4NO_3 — 52% Mg — 48%	—	2300	0,582	218	440
12	NH_4ClO_4 — 71% Mg — 29%	—	2440	—	200	314
13	KNO_3 — 89,2% C_nH_{2n} — 10,8%	—	450*	0,428	120	530
	10) *Жидкие топлива*					
14	HNO_3 C_nH_{2n}	1,35	1450	0,45	239	—
15	$C(NO_2)_4$ C_nH_{2n}	1,47	1700	0,468	262	—
16	O_2 C_nH_{2n}	1,02	2270	0,428	290	720
	11) *Смеси жидких и твердых компонентов*					
17	$C(NO_2)_4$ — 82,3% B — 17,7%	—	2190	0,42	283	—
18	$C(NO_2)_4$ — 64,5% Al — 35,5	1,91	1800	0,42	256	—
19	$C(NO_2)_4$ — 80,5% $B_{10}H_{14}$ — 19,5%	1,44	2150	0,48	300	—
20	B — 31,5% O_2 — 68,5%	—	3180	0,248	264	320
21	Al — 54,3% O_2 — 45,7%	—	2200	0,248	220	220

*Or 770 kcal/kg for K_2O in the solid state. [Key on next page]

	Heating yield, kcal/kg	Specific gas production, liters/kg	Specific impulse ($p/p_0 = 50$), sec
(1)	1320	460	220
(2)	1250	510	242

Thus, when metallic combustibles are used in compounds with solid oxidizers, it is better to have the process go toward formation of the metal oxide and hydrogen than toward formation of water and the metal oxide.

It is interesting to note that the introduction of metals into a propellant mixture where the oxidizer is liquid oxygen does not raise but lowers the specific impulse. In contrast to this, aluminum and boron additives raise the specific impulse on injection into compositions with ammonium perchlorate.

This will be seen from the following examples:

Combustible	Specific impulse ($p/p_0 = 50$), sec	
	NH_4ClO_4	O_2
Rubber	232	290
Aluminum	242	222
Boron	254	264

Combustion of propellants containing liquid oxygen, aluminum, and boron results in formation of a small gaseous phase, so that the effectiveness of such fuels is lower than that of fuels based on hydrocarbons and oxygen in spite of their high heating yield.

The gaseous phase for the ammonium perchlorate/aluminum propellant with its high heating yield is comparatively large, so that the propellant develops a higher specific impulse than the ammonium perchlorate/rubber propellant.

In the opinion of Crook [18], a specific impulse of the order of 230 sec corresponds to the stoichiometric composition of the ammonium perchlorate/rubber or polyurethane propellant. The addition of aluminum in dust or powder form in quantities up to 20% increases the impulse by 7% for any composition. By combining a nitro binder and an aluminum additive with ammonium perchlorate, we may raise the specific impulse to 250 sec, or to 240 sec by combining them with polyurethane resin, aluminum, and perchlorate.

Let us attempt to evaluate the limiting specific-impulse value for metallic-combustible propellants. To produce a high specific impulse, it is necessary to have high heating yields and a large specific volume of the working fluid. Hydrogen in the combustion products increases the gas yield considerably.

Let us consider the systems $Mg + 1/2 O_2 + nH_2$; $Be + 1/2 O_2 + nH_2$ and $2Al + 1-1/2 O_2 + nH_2$, the theoretical characteristics of which are presented in Table 167.

The limiting specific-impulse value in the case of metallic combustibles runs to 350-420 sec if the oxidizer is oxygen and the working fluid is hydrogen. In practice, this value is considerably lower for known oxidizers because of the heat expended on decomposition of the oxidizer and the somewhat less than optimum proportions between the oxygen and hydrogen.

Naturally, the metal-hydrogen-oxygen system may be regarded only from theoretical standpoints, since it is not feasible in practice.

The specific impulse is about 280 sec for hypothetical systems such as solidified liquid oxidants with hydrocarbons and metals, e.g., boron with tetranitromethane. However, the use of liquid oxidants in solid propellants would require some method of solidifying them. The specific impulse that can be obtained with the use of

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TABLE 167

Calculated Characteristics of Hypothetical Propellant Mixtures Based on Metals, Hydrogen, and Oxygen

1) Состав	2) Теплопроизводительность, ккал/кг	3) Удельный объём, л/кг	4) Теплоемкость (C_p), ккал/кг·град	5) Температура горения, °C	6) Удельный импульс (p/p_0 = 50), сек.
I. Топливные системы с магнием					
$Mg + \frac{1}{2}O_2$	3650	0	0,3	—	0
$Mg + \frac{1}{2}O_2 + 2H_2$	3300	1050	0,74	4500	310
$Mg + \frac{1}{2}O_2 + 3H_2$	3150	1450	0,93	3400	320
$Mg + \frac{1}{2}O_2 + 4H_2$	3020	1870	1,11	2700	340
$Mg + \frac{1}{2}O_2 + 5H_2$	2900	2250	1,25	2300	325
$Mg + \frac{1}{2}O_2 + \frac{1}{2}N_2$	2680	205	0,325	—	185
$Mg + \frac{1}{2}O_2 + N_2$	2140	330	0,33	6500	208
$Mg + \frac{1}{2}O_2 + 2N_2$	1520	460	0,33	4700	210
$Mg + \frac{1}{2}O_2 + 4N_2$	950	590	0,345	2750	142
II. Топливные системы с алюминием					
$Al + 1\frac{1}{8}O_2 + 5H_2$	3600	1600	—	4900	315
$Al + 1\frac{1}{2}O_2 + 10H_2$	3300	1850	—	—	338
$Al + 1\frac{1}{8}O_2 + 15H_2$	3050	2570		2700	340
$Al + 1\frac{1}{2}O_2 + 20H_2$	2630	3200		1710	330
III. Топливные системы с бериллием					
$Be + \frac{1}{2}O_2$	5800	0	0,3	—	0
$Be + \frac{1}{2}O_2 + H_2$	5400	830	0,65	8300	373
$Be + \frac{1}{2}O_2 + 2H_2$	5000	1540	0,95	5250	405
$Be + \frac{1}{2}O_2 + 3H_2$	4750	2150	1,2	3900	415
$Be + \frac{1}{2}O_2 + 4H_2$	4400	2700	1,44	3050	408
$Be + \frac{1}{2}O_2 + 5H_2$	4150	3200	1,64	2500	403
$Be + \frac{1}{2}O_2 + 6H_2$	3900	3600	1,82	2150	395
IV. Системы с водородом, кислородом и фтором					
$H_2 + F_2$	3190	1120	—	—	395
$H_2 + \frac{1}{2}O_2$	3215	1230	—	—	355

1) Composition; 2) heating yield, kcal/kg; 3) specific volume, liters/kg; 4) heat capacity (C_p), kcal/kg·degree; 5) combustion temperature, °C; 6) specific impulse $(p/p_0 = 50)$, sec; I) Propellant systems with magnesium; II) propellant systems with aluminum; III) propellant systems with beryllium; IV) systems with hydrogen, oxygen, and fluorine.

solid propellants depends on the combustion-chamber pressure and the nozzle-section pressure. Pressures from 35 to 70 atm are most frequently used in solid-propellant engines. With the engine operating in space,* at $p_0 = 0$, the thermal efficiency will not reach its maximum value, i.e., unity, as might be expected in accordance with the formula

$$\eta_t = 1 - \left(\frac{p_0}{p}\right)^{\frac{k-1}{k}}$$

because outflow from the nozzle is not ideal. Flow breakaway takes

place at some value of p_0, which does not reach $p_0 = 0$.

TABLE 167a

Variation of Calculated Specific Impulse of Ammonium Perchlorate/ Polyethylene Propellant Mixture

1) Условия работы двигателя	Удельный импульс при давлении в камере, сек. 2)		
	40 am	50 am	70 am 3)
4) У земли . .	228	232	240
5) В пустоте .	268	272	282

1) Operating conditions of engine; 2) specific impulse, sec; 3) atmospheres; 4) at surface; 5) in space.

TABLE 168

Characteristics of Solid Propellants Based on Ammonium Perchlorate and Resin as Functions of Oxidizer Content [6]

1) Показатели	2) Содержание окислителя				
	70%	75%	80%	85%	90%
3) Теплопроизводительность, ккал/кг	698	864	1010	1050	1260
4) Плотность при 20°	1,60	1,64	1,70	1,76	1,77
5) Удельный импульс при 70,3 am, сек:					
а) у поверхности земли	180	192	204	215	230
б) в пустоте	211	226	239	251	272

1) Property; 2) oxidizer content; 3) heating yield, kcal/kg; 4) density at 20°; 5) specific impulse at 70.3 atm, sec: a) at the surface; b) in space.

With the engine operating in space, however, the specific impulse increases by approximately 15%. This can be seen from the data listed in Table 167a.

We have considered possible recipes for solid propellants at the stoichiometric composition, without taking fueling and operational possibilities into account.

In practice, solid-propellant recipes differ from the stoichiometric compositions, at which the maximum evolution of energy could be obtained. This is a result of the fact that the combustibles and binders must, for a number of technical reasons, be used in quantities larger than are necessary for complete combustion. The literature data giving recipes for mixed solid propellants are extremely incomplete; nor is detailed information available on the production processes used for them. Apparently, not all of the characteristics of the recipes given in the literature are sufficiently trustworthy. Table 168 shows

heating yields and specific impulse as functions of the contents of
ammonium perchlorate and resin in the fuel. Table 169 gives certain
known solid-propellant recipes.

TABLE 169

Characterization of Certain Casting Solid-Propellant
Compositions [6, 20, 21]

1) Состав топлива		2) Плот- ность при 20°	3) Удельный импульс, сек.	
			4) у земли	5) в пустоте
Перхлорат аммония — 75% Полиуретан — 25%	6)	1,84	12) 226 (35 am)	266
Перхлорат аммония Полибутадиен Акриловая смола Алюминиевая пудра	7)	1,87	230—238 (40 am)	250—280
Нитрат аммония — 80%* Синтетический каучук—10% Сажа — 7—9% Добавки — 1—3%	8)	—	185 (70 am)	216
Перхлорат калия — 76,5% Битум — 23,5%	9)	1,77	186 (140 am)	—
Перхлорат аммония — 74% Полисульфидный каучук —26%	10)	1,70	—	—
Перхлорат аммония — 65—70% Нитрополиуретан — 25—30% Алюминий — 5—10%	11)	—	250 (50 am) 263 (68 am)	—

*Molded compound.

1) Compositon of propellant; 2) density at 20°; 3) specific
impulse, sec; 4) at surface; 5) in space; 6) 75% ammonium
perchlorate and 25% polyurethane; 7) ammonium perchlorate,
polybutadiene, acrylic resin and aluminum dust; 8) 80%
ammonium nitrate,* 10% synthetic rubber, 7 to 9% carbon
black and 1 to 3% of additives; 9) 76.5% potassium per-
chlorate and 23.5% asphalt; 10) 74% ammonium perchlorate
and 26% polysulfide rubber; 11) 65 to 70% ammonium per-
chlorate, 25 to 30% nitropolyurethane and 5 to 10%
aluminum; 12) atmospheres.

As a comparison example, we cite the composition of a typical
rocket powder: 50.0% nitrocellulose; 41.0% nitroglycerine and 9.0%
ethylcentrolite; its heating yield is 965 kcal/kg and its specific
impulse is 220 sec. A Pb_3O_4 additive is sometimes used to improve the
combustion characteristics [18b].

A polyurethane propellant is used in the "Polaris" intermediate-
range ballistic missile. The specific impulse may be increased by

using polymers containing nitro groups instead of ordinary resins and rubbers, since then a value of α close to the optimal is reached if an adequate quantity of binder is supplied.* Another way to raise the specific impulse (by 10-20 units) is the introduction of a certain quantity of substances such as aluminum and boron. Thus, the addition of 15-20% of aluminum dust to almost any composition increases the specific impulse by 14-16 units.

Solid mixed propellants are characterized by relatively low combustion temperatures as compared with the propellants used in liquid reaction-thrust engines (Table 170).

The relatively low combustion temperature makes it possible to use an uncooled nozzle for the engine if it is made from special heat-resistant alloys and ceramics. At the same time, the introduction of additives that raise the heating yield and, consequently, the combustion temperature, requires development of more highly refractory nozzles. It is indicated in the literature that beryllium, boron, magnesium, and lithium additives are introduced into solid propellants to raise their efficiency [21]. Among the substances noted above, boron has attracted special attention, and attempts have been made to use it in elementary form and in the form of its hydrogen compounds, as well as in high-molecular-weight compounds that might serve simultaneously as binders for oxidants [23].

A number of difficulties confront the use of boron. This results from the fact that elementary boron burns poorly, while its compounds with hydrogen, such as decaborane, are chemically unstable in mixtures with oxidizers. Hence it is desirable to introduce boron in the form of its more or less stable compounds.

The use of boron in high-molecular-weight compounds used as binders may give a rise of the order of ten units in the specific

TABLE 170

Recipes and Combustion Temperatures for Solid-Propellant Compositions [21, 22]

1) № п/п	2) Рецептура	3) Плотность при 20°	4) Температура горения, °C
1	NH₄ClO₄ — 65% 5) Полиэфир — 35%	1,62	1690
2	NH₄ClO₄ — 65% 6) Полисульфидэпоксидная смола — 35%	1,63	1750
3	NH₄ClO₄ — 75% 7) Полисульфидэпоксидная смола — 25%	1,70	2550
4	NH₄ClO₄ — 75% 8) Смолы — 25%	—	2200
5	NH₄ClO₄ — 52,5% KClO₄ — 17,5% 9) Полисульфидэпоксидная смола — 30%		2350
6	KClO₄ — 76,5% 10) Битум — 23,5%	1,77	2000

1) No.; 2) recipe; 3) density at 20°; 4) combustion temperature, °C; 5) polyester; 6) polysulfide epoxy resin; 7) polysulfide epoxy resin; 8) resins; 9) polysulfide epoxy resin; 10) asphalt.

impulse, and this is of definite interest. Thus, for example, a three-unit increase in specific impulse (above 310 sec in space) results in a 470-km increase in range for a ballistic rocket designed for a range of 11,000 kilometers [6].

5. SPECIAL POINTS IN APPLICATION OF BORON AND METALS IN SOLID PROPELLANTS

Boron compounds. The introduction of elementary boron, metals or hydroborons, which do not possess plastic properties, into a solid-propellant composition may result in an excessively large drop in the mechanical strength of the charge, while the use of hydroborons in solid propellants in the form of a simple mechanical mixture is limited by their sensitivity to oxygen and moisture. In view of this, it is desirable to have more stable boron-containing polymers. These may be of several types [24].

1) Inorganic polymers produced by pyrolysis of lower hydroborons.

Thus, decaborane $B_{10}H_{14}$ can be polymerized to higher hydrides. The terminal hydrogen atoms react first, forming compounds of the type $(B_{10}H_{12})_2$ and then polymers of the composition $(B_{10}H_{12})_x$ and $(BH_n)_x$.

On heating, solid diborane diammoniate $H_2B(NH_3)_2BH_4$ may undergo transformation into a more complex high-molecular substance with polymer chains [24]:

$$BH_2 - NH_2 \ldots BH_2 - NH_2 \ldots$$
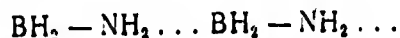
There is a possibility of polycondensation between hydroborons and hydrazines; thus, a high-molecular substance of the following type is formed from decaborane and hydrazine:

$$xB_{10}H_{14} + xN_2H_4 \xrightarrow{-H_2} (- NH - NH - B_{10}H_{12} -)_x$$
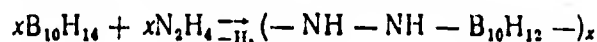
2) Organic polymeric compounds are produced by various methods:

A. Cyclotrimethylboroctane [25] is formed when trimethylborane $(CH_3)_3B$ is heated in an autoclave at $400\text{-}600^\circ$:

$$
\begin{array}{ccc}
 & CH_2 & \\
 & \diagup \quad \diagdown & \\
CH_3 - B & & B - CH_3 \\
| & & | \\
CH_2 & & CH_2 \\
| & & | \\
CH_3 - B & & B - CH_3 \\
 & \diagdown \quad \diagup & \\
 & CH_2 &
\end{array}
$$
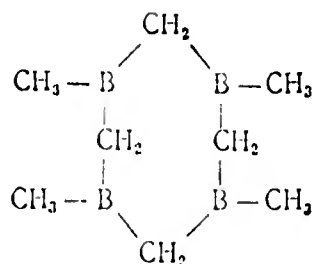
as are high-molecular polymers of the composition

$$
\left[\begin{array}{c} - B - CH_2 - CH_2 - B - \\ | \qquad\qquad | \\ CH_3 \qquad\qquad CH_3 \end{array} \right]_x
\text{and}
\left[\begin{array}{c} CH_2 - CH_2 \\ \diagup \qquad \diagdown \\ - CH_2 - CH_2 - B \qquad\qquad B - \\ \diagdown \qquad \diagup \\ CH_2 - CH_2 \end{array} \right]_x
$$
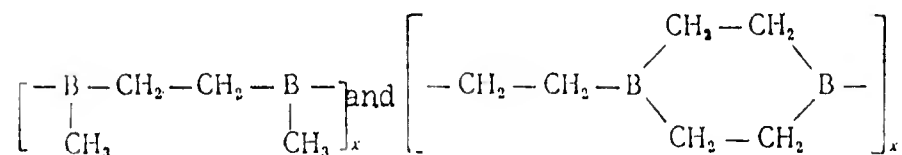
Alkyl boranes of the types B_2H_5–R and $B_{10}H_{13}$–R split off hydrogen on heating to form resin-like products. Hydroborons combine readily at their double and triple bonds, and it is upon this that the preparation of their alkyl derivatives is based.

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In an analogous manner, addition of decaborane to high-molecular weight compounts containing double bonds is also possible; e.g., on addition to butadiene rubber:

$$[-CH_2-CH=CH-CH_2-]_x + xB_{10}H_{14} \rightarrow [-CH_2-CH_2-CH_2-CH_2-]_x$$
$$\underset{B_{10}H_{13}}{\overset{|}{}}$$
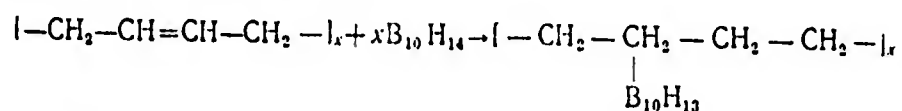
B. Hydroborons form compounds with primary and secondary amines and diamines, as well as with hydrazine derivatives, which can be transformed into high-molecular compounds under certain conditions, with hydrogen split off. For example [24]:

$$B_2H_6 + H_2NC_2H_4NH_2 \xrightarrow{-H_2} BH_3 \cdot H_2N - C_2H_4 - NH_2 \cdot BH_3 \rightarrow$$
$$\rightarrow [-BH_2 \ldots NH_2 - C_2H_4NH - BH_2 \ldots]_x$$
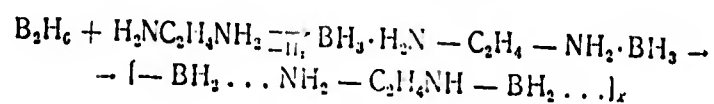
Dimethylamine forms a resinous polymer of the following composition with diborane:

$$[(CH_3)_2NBH_2]_x.$$
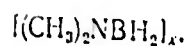
Decaborane reacts with nitriles to form addition products of the composition

$$B_{10}H_{14} \cdot 2RCN.$$
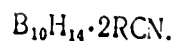
A similar compound may be produced with polyacrylonitrile:

$$\begin{bmatrix} -CH_2-CH- \\ | \\ CN \end{bmatrix}_x + B_{10}H_{14} \rightarrow$$
$$\rightarrow \begin{bmatrix} -CH_2-CH- \\ | \\ C \equiv N \ldots B_{10}H_{14} \ldots \end{bmatrix}_x$$
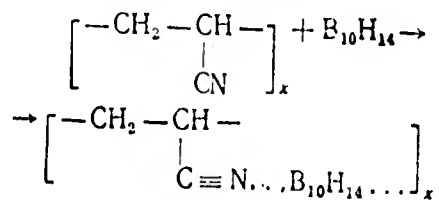
C. Resinous polymers of the type $[R_2PBH_2]_n$, containing phosphorous in addition to boron, have been synthesized.

Thus, a polymer of the composition

$$[(CH_3)_3PBH_2]_x,$$
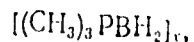
forms on heating of the borine complex; it possesses thermoplastic properties.

Pentaborane B_5H_9 and trialkylphosphine $(R)_3P$ form resins that are

stable to moisture and oxygen and retain their properties on heating to 500°; they have molecular weights of the order of 12,500 [26, 27, 28].

Silicon-organic compounds of the following type have been reported:

$$RB [CH_2Si (R)_2 OS (OR)_3]_x.$$
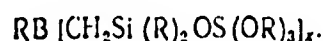
In the USA in 1957, the cost of one ton of alkyl boranes (ethyl pentaborane and ethyl decaborane) was $30,000, while in 1959-1960 it had been reduced to 1450-2200 dollars; the cost of a conventional solid propellant is about $10,000 [29].

Combustion processes of metals. Burning metals used as components in solid propellants is a more complex problem than setting up combustion of organic compounds. It may be assumed that the combustion of metals used in solid rocket propellants takes place by a diffusion mechanism. The temperature of the flame surrounding the metal particle is higher than the equilibrium adiabatic combustion temperature of the propellant in question. It appears that equilibrium intervenes after condensation of the metal oxide in subsequent stages of combustion in the engine chamber.

Complex compounds containing metals may be completely oxidized or, on the other hand, they may decompose into the metal and other products. Combustion of the metal particles formed during this process takes place by the diffusion mechanism. It appears that combustion of most alkyl compounds of metals takes place by this mechanism. The temperatures that can be attained on combustion of metals are limited by the vaporization temperature of the metal's oxides, irrespective of whether the oxide decomposes on vaporization or not. If the combustion products of metals diffuse into cooler zones, they condense. The vaporization or condensation temperature varies as a function of pressure,

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and for those compounds that decompose the attainable combustion tem-
perature will also depend on the dissociation temperature. Thus, the
combustion temperature stabilizes as a result of an equilibrium vapori-
zation and dissociation process:
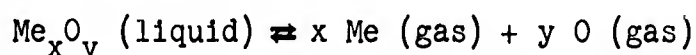
$$Me_xO_y \text{ (liquid)} \rightleftharpoons x \text{ Me (gas)} + y \text{ O (gas)}$$
$$K_p = (Me)^xO^y[p/\Sigma m]^{x+y},$$

here, Me is the metal, Σm is the total number of moles of gas, and
p is the pressure.

Diffusive combustion of metallic combustibles can be described
by means of the diagram shown in Fig. 219.

The heat propagates from the flame front toward the surface of
the particle. The combustible vaporizes or sublimates and diffuses
from the particle surface toward the flamefront. Oxygen diffuses to-
ward the particle surface.

A more complex theory that takes kinetics into account for a
finite reaction rate and does not adopt an ignition range would not
significantly change the basic pattern and, in actuality, would predict
the same combustion rate as the simplified theory.

Another departure peculiar to diffusive combustion of a metal
is the formation of condensed oxides, which does not occur in com-
bustion of organic substances.

For all alkaline earths, the oxide molecules of the metals are
volatile substances, with the exception of beryllium oxide BeO, which
decomposes into the elements on evaporation.

The oxidizer and combustible begin to react before the oxygen
concentration required for stoichiometric composition has been reached,
so that the majority of metals react in a reducing medium.

Boron oxides form on combustion of boron in a flame. At high
temperature, boron oxides undergo complex transformation, including
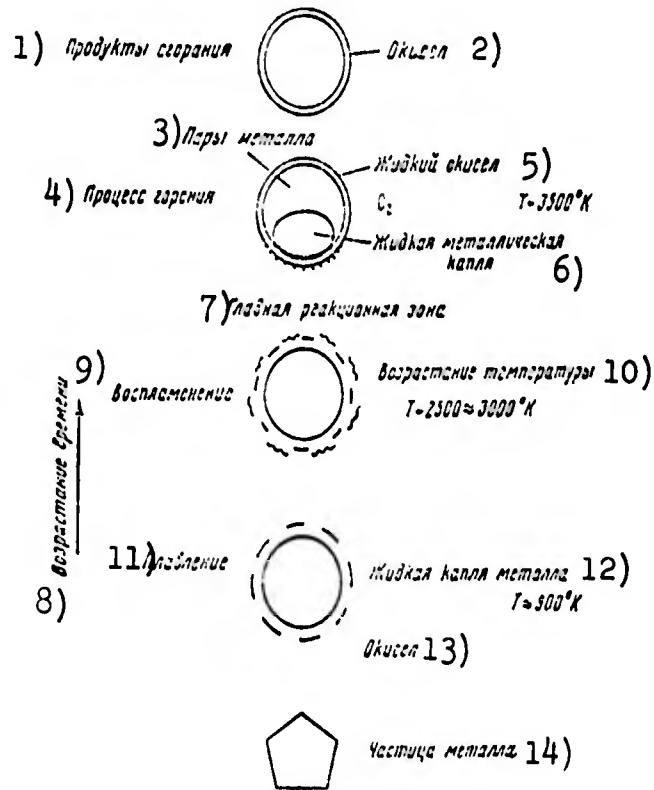
Fig. 219. Diagram of combustion of metallic
particle; 1) Combustion products; 2) oxide;
3) metal vapor; 4) combustion process; 5)
liquid oxide; 6) liquid metal drop; 7) main
reaction zone; 8) increasing time; 9) igni-
tion; 10) increase in temperature; 11) fusion;
12) liquid metal drop; 13) oxide; 14) metal
particle.

dissociation, reduction, and oxidation:

$$2B + 1\tfrac{1}{2}O_2 \rightarrow B_2O_3; \quad B_2O_3 \rightleftarrows B_2O_2 + O$$
$$B_2O_2 \rightleftarrows 2BO \qquad 2BO + O \rightarrow B_2O_3$$
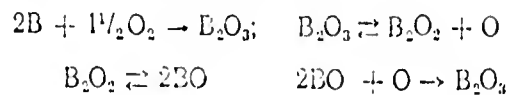
The dissociation of B_2O_3 into B_2O_2 and BO below a temperature of
$2500^\circ K$ does not exceed 5%.

The possibility of dissociation of Al_2O_3 with formation of AlO
and Al_2O at the flame temperature has been demonstrated in the com-
bustion of aluminum; Al_2O is a product of combustion of aluminum in
a reducing atmosphere, while AlO is a product formed in an oxidizing
atmosphere. It has been shown by thermodynamic calculations that the
decomposition of Al_2O_3 is quite considerable near the boiling point.

In the presence of CO and $H_2Al_2O_3$, it begins to show considerable dissociation at a temperature of about 3000°.

The heat of formation of Al_2O (gas) is $+34$ kcal/mole, and that of AlO is $+63$ kcal/mole.

The boiling point of the metal and the oxide formed may exert an influence on the metal's rate of combustion. Thus, if the metal's boiling point is higher than that of the oxide, the oxide coats the surface of the metal particle and blocks access of oxygen, and combustion is inhibited (e.g., titanium and boron). If the boiling point of the oxide is higher than that of the metal, the metal will vaporize and its vapors will diffuse through the oxide to mix with the oxygen and burn (aluminum, magnesium, beryllium). In this case, the flame front will be closer to the metal surface, and combustion will proceed at a higher rate.

Below we list the compositions of oxides that may form as a result of adiabatic combustion of metals and hydrides [30].

Combustible	Products of adiabatic combustion
Pentaborane B_5H_9	B_2O_3(liq, gas) BO, B, BH
Aluminum Al	Al_2O_3(solid, liq, gas), Al_2O, AlO, Al
Boron B	B_2O_3 (liq, gas), BO, B
Magnesium Mg	MgO (solid, liq)
Beryllium Be	BeO (solid, liq)

In addition, the combustion products of the propellant may contain O_2, N_2, NO, O, N, OH, H_2O, CO, and CO_2.

The most important factor influencing the oxidation rate of boron in combustion is the withdrawal of boron oxide, which coats the particles of unburned boron and thereby impedes further combustion, from the reaction zone. Depending on temperature in the range up to 3000°, we observe several combustion mechanisms for boron, as determined by the form of the boron oxide — whether it is in the solid, liquid, or
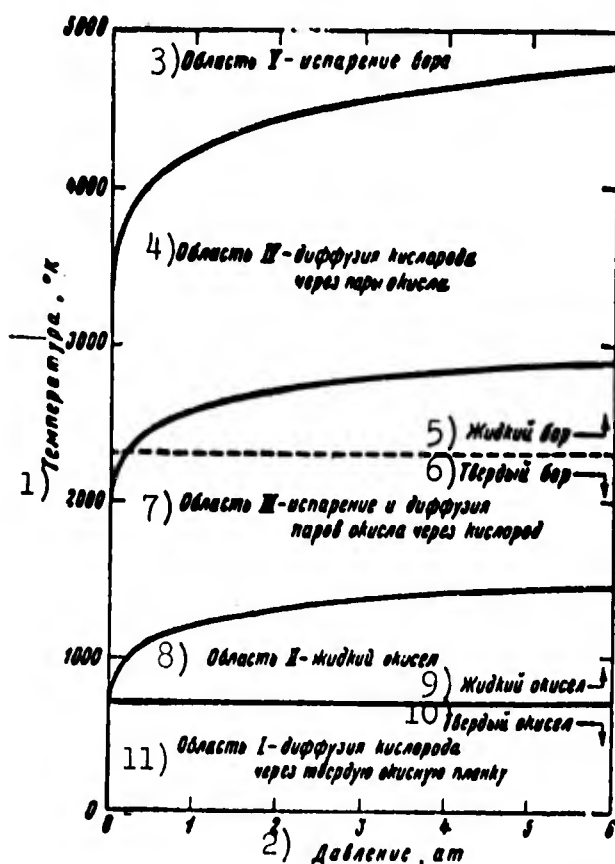
Fig. 220. General pattern of combustion of elementary boron as a function of temperature and pressure. 1) Temperature, °K; 2) pressure, atm; 3) region V – evaporation of boron; 4) region IV – diffusion of oxygen through oxide vapor; 5) liquid boron; 6) solid boron; 7) region III – evaporation and diffusion of oxide vapors through oxygen; 8) region II – liquid oxide; 9) liquid oxide; 10) solid oxide; 11) region I – diffusion of oxygen through solid oxide film.

gaseous state.

Figure 220 shows the various states of boron oxide as a function of temperature and pressure [31].

In the first stage of the reaction, in which solid boron oxide forms, oxidation proceeds slowly. The rate of the reaction is limited by the supply of oxygen through the solid film to the surface of the boron.

Liquid boron oxide ($723°K$) forms in the second stage; under the appropriate conditions, it may drain from the particle surfaces. The

thickness of the liquid oxide film varies over time until equilibrium has been established between the viscosity of the liquid and its surface tension. In this region, the rate of the process is determined by the elimination of boron oxides from the surfaces of the particles of elementary boron. Raising the temperature to $1100^{\circ}K$ results in removal of the boron oxide film from the reaction zone both by drainage and by evaporation.

TABLE 171

Combustion Temperature of Hydrocarbons with Various Contents of Metal in Air

1) Горючее	2) Температура горения, °K	
	a = 0,8	a = 1,0
3) Октен	2150	2300
Октен + 40% Mg . . .	2350	2550
Октен + 80% Mg . . .	2850	3100
4) Магний	3100(a=0,5)	—
3) Октен + 40% Al	—	3050
Октен + 80% Al	—	2700
5) Алюминий	3200	3350
3) Октен + 40% B	—·	2500
Октен + 6.% B	—	2600
6) Бор	2700	2800
7) Пентаборан B₅H₉	2500	2700

1) Combustible; 2) combustion temperature, $^{\circ}K$; 3) octene; 4) magnesium; 5) aluminum; 6) boron; 7) pentaborane.

At a certain temperature (third stage), the film thickness depends only on evaporation rate, and it is this factor that determines the oxidation rate.

As the temperature rises, the thickness of the liquid boron oxide film diminishes, and at a certain temperature the oxide film vanishes completely from the surface of the solid boron. In fact, the oxidation rate of the boron in the fourth stage depends on the rate of diffusion of gaseous oxygen through the boron oxide vapors. The rate of diffusion of gaseous oxygen into the reaction zone is another process that determines the oxidation-reaction rate in the fourth region. If the temperature increases even further, elementary boron vapor will appear in the reaction zone (fifth region). As a result, the fraction of elementary boron undergoing oxidation in the vapor phase increases with increasing temperature. A boron liquid phase appears at $2300^{\circ}K$.

Thus, a film of boron oxide is formed on the surface of the ele-

mentary boron during the heating process when powdered boron is burned. On further heating of the particles, the boron oxide evaporates to leave the boron surface completely clean and in contact with the oxygen. Obviously, any measures that help accelerate evaporation of the boron oxide should also promote the combustion reaction. Thus, for example, the introduction of about 1% of water vapor into the gaseous oxygen nearly doubles the rate of combustion of elementary boron at a temperature of $2340^{\circ}K$.

The theoretical characteristics of exotic propellants are of interest from the standpoint of ascertaining the potential of propellant compositions that have been suggested but not yet tested, as well as from the standpoint of a reference for evaluation of experimental results [32, 33]. Calculations were carried out for the combustion of metals and suspensions of metals in hydrocarbons for an air atmosphere. Some of these data are of interest for comparative evaluation of the results of combustion of hydrocarbon combustibles with various quantities of metal (Table 171).

The combustion temperature of boron is 500° higher than that of octene, while those of aluminum and manganese are approximately 1000° higher than that of octene [30].

6. COMBUSTION RATE AND EXPLOSIVE PROPERTIES OF SOLID PROPELLANTS

Explosive properties. Mixed propellants contain sufficient oxidizers to make them ignite and burn readily. The heating yield of solid propellants lies between 900 and 1300 kcal/kg, i.e., it may be higher than those of explosives such as trinitrotoluene (heat of explosion 1000 kcal/kg). Under certain conditions, mixed solid propellants may show explosive properties manifested in combustion going over into detonation or detonation occurring on impact, as in firing of cartridges, etc. It is also important to know what factors may give

rise to detonation.

The sensitivity of solid-propellant compositions to various disturbances depends on a whole series of factors:

a) on the nature of the oxidizer (ammonium perchlorate or ammonium nitrate);

b) on the nature of the combustible for a given oxidizer;

c) on the fineness to which the components are divided and the intimacy with which they are mixed;

d) on the density of the mixture (the density of the cast or pressformed charge);

e) on the initial temperature of the charge, and so forth.

The sensitivity of perchlorate compositions — both in powder form and in the form of individual charges weighing from 1 to 1050 kg, and containing from 57 to 88% of perchlorate [31] — to disturbances of varying severity was investigated; the disturbances included shock, friction, the explosion of a standard No. 8 detonator and a detonator assisted by a 5-gram tetryl cap. It was established as a result of the investigations that susceptibility to a capsule detonator depends on the volume ratio of combustible to oxidizer in the mixture. The higher the volume ratio for a given weight ratio, the lower will the sensitivity be.

Under the operating conditions of solid-propellant rockets, poly-sulfide-perchlorate propellants containing no more than 74% of oxidizer represent an explosion hazard. Solid rocket propellants based on ammonium perchlorate and polyester resin represent an explosion hazard under operational conditions if the oxidizer content does not exceed 80 or 85% when rubber has been taken as a combustible and binder.

Combustion rate. The combustion of solid-propellant charges takes

place by parallel layers. The thrust P developed by the engine depends on combustion rate in accordance with the formula

$$P = V\rho S\overline{p},$$

where ρ is the density of the propellant, S is the area of the propellant charge, $\underline{p}$ is the specific impulse expressed in kilograms per 1 kg of propellant burned, in sec, and V is the linear combustion rate.

The linear combustion rate depends upon the pressure at which the process is unfolding, in accordance with the law

$$V = b p^n \quad \text{or} \quad V = a + b p^n,$$

where $\underline{a}$, $\underline{b}$, and $\underline{n}$ are constant characteristics of the propellant as determined by experiment [34].
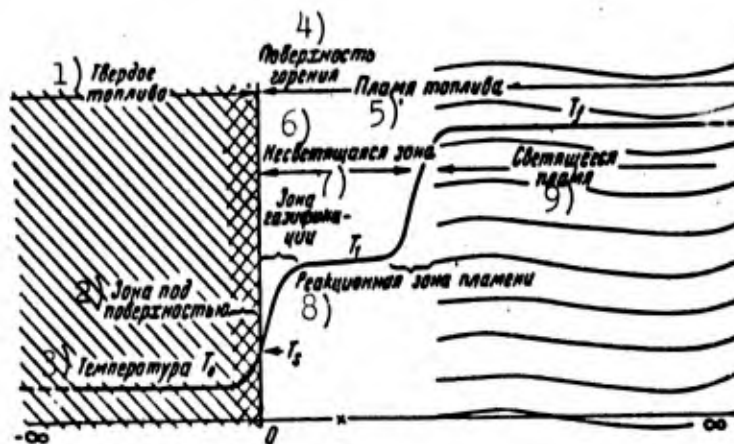
Fig. 221. General diagram of solid-propellant combustion. 1) Solid propellant; 2) subsurface zone; 3) temperature T_0; 4) combustion surface; 5) propellant flame; 6) nonluminous zone; 7) gasification zone; 8) reaction zone of flame; 9) luminous flame.

Depending on the composition of the propellants used, the combustion rate at a pressure of 70 atmospheres varies from 2.5 to 12.7 mm/sec with exponents $\underline{n}$ from 0.1 to 0.4 [35].

The combustion rate also depends on the initial temperature of the charge and its heating yield. The variation of combustion rate as a function of initial temperature is about 5% for each 10°. The follow-

ing approximate relationship prevails between the heating yield H
and combustion rate:

$$\lg V = 1.47 + 0.846 \frac{H}{1000}$$

Combustion of a solid propellant is a multistage process [36].
The following events occur due to the influx of heat from the com-
bustion zone:

a) heating of the substance to the temperature at which physical
and chemical changes begin;

b) evaporation or foaming of the solid-propellant components
due to partial decomposition;

c) total gasification of the propellant components, i.e., their
transition into the gaseous state due to evaporation or thermal de-
composition;

d) preignition reactions in advance of ignition;

e) reactions in the flame, which leads to formation of the final
products.

A general diagram of the combustion processes appears in Fig. 221.
The combustion process of solid propellants takes place in the gaseous
phase, but it is preceded by a stage in which the solid phase is gasi-
fied; this phase is slower than either ignition or combustion of the
vapor. As a result, the gasification rate determines the over-all
combustion rate in much the same way as the evaporation rate of liquid
combustibles determines their combustion rate. As a result, the com-
bustion rate depends on the rate of gasification of the propellant
components and the heat flow from the flame zone, which will be higher
the higher the heating yield. The combustion rate is determined by
the nature of the oxidants used. At a given combustion temperature,
the combustion rate increases in the following series as a function of
the oxidizer employed:

$$NH_4NO_3 < NH_4ClO_4 < KClO_4$$

and depends on the decomposition temperature of the oxidizers.

Decomposition of the oxidizers takes place at temperatures approximately as follows:

$KClO_4$ . . . . 500—530°
NH_4ClO_4 . . 300—350°
NH_4NO_3 . . 243—361°
$NaNO_3$ . . . 255—370°
KNO_3 . . . . 286—300°

On heating, decomposition of ammonium nitrate takes place in accordance with the equations

$$NH_4NO_3 \nearrow 0,5NO_2 + 2H_2O + 0,75N_2$$
$$\searrow N_2 + 0,5O_2 + 2H_2O$$
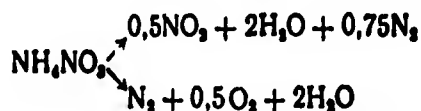
The activation energy of the decomposition process is 40,500 cal/ /mole [35].

The thermal decomposition of ammonium perchlorate takes place in accordance with the equations

$$NH_4ClO_4 \nearrow^{<300°} 1,5H_2O + 0,5N_2 + HCl + 1,25O_2$$
$$\searrow^{>300°} 2H_2O + 0,5N_2 + 0,5Cl_2 + O_2$$
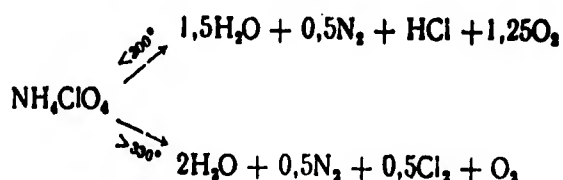
Potassium perchlorate decomposes into potassium chloride and oxygen:

$$KClO_4 \xrightarrow{>500°} KCl + 2O_2.$$
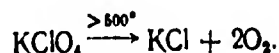
The activation energy of the decomposition process is 60,800 cal/mole.

In preparations containing the most thermostable oxidizers, the combustion rates are higher.

For compositions based on ammonium perchlorate, the following combustion rates for 140 atm are given for comparison with nitro-glycerine powder:

1) NH_4ClO_4 — 75%   7.6 mm/sec
   Resins — 25%

2) Nitrocellulose — 77%
   Nitroglycerine — 22%   8.4 mm/sec
   Ethylcentralite — 1%

The degree to which the oxidizer is pulzerized exerts a strong influence on combustion rate. Thus, the combustion rate of a composition based on ammonium perchlorate varies as follows as a function of perchlorate-particle size at 70 atm:

Oxidizer particle size, μ	Combustion rate, mm/sec
1 – 2	40
35	20

No less important an influence is exerted by combustible particle size on combustion rate, assuming that this combustible does not melt, but is mixed with the oxidizer in the powdered state.

If the propellant contains metal particles, they enter the vapor phase on gasification of the propellant; here, they ignite at temperatures higher than the gasification temperature and undergo combustion. But the ease of ignition is determined by particle size, since the finer particles are heated to the ignition temperature more rapidly. The smallest spark-discharge energy that will ignite a dust cloud of the metal in air is taken as a quantitative characteristic of ease of ignition.

Minimum spark-discharge energy, joules	0.2	0.033	0.025
Particle size, μ	90	70	40

When the particle size is approximately halved, the ignition energy is reduced almost by a factor of 10.

As the carbon-particle size is varied from 0.1 to 0.001 mm, the combustion time drops by a factor of approximately 10,000.

In addition to the normal combustion rate, the erosional com-

TABLE 172

Characteristics of Solid Propellants

1) Обозначение заряда	2) Топливо	3) Средний размер частиц окислителя, μ	4) Плотность при 20°	5) Температура горения, °C	6) Средний молекулярный вес продуктов горения
A 7)	NH_4ClO_4 — 65% Полиэфир — 35%	24—30	1,62	1690	21
Б 8)	NH_4ClO_4 — 65% Полисульфид + эпоксидная смола —35%	24—30	1,63	1750	22
C 9)	NH_4ClO_4 — 75% Полисульфид+ эпоксидная смола— 25%	24—30	1,70	2550	25
P 10) 11)	NH_4ClO_4 — 50% $KClO_4$ — 20% Полисульфид — 22,5% Эпоксидная смола — 7,5%	24—30	1,74	2220	26

1) Designation of charge; 2) propellant; 3) average oxidizer-particle size, μ; 4) density at 20°: 5) combustion temperature, °C; 6) average molecular weight of combustion products; 7) 35% polyester; 8) 35% of polysulfide + epoxy resin; 9) 25% of polysulfide + epoxy resin; 10) 22.5% polysulfide; 11) 7.5% epoxy resin.

TABLE 173

Erosional and Normal Combustion Rates of Solid Propellants [37, 38]

1) Топливо	2) Характеристика потоков газа		5) Скорость горения (эрозионная), мм/сек		8) Скорость горения с торца, мм/сек
	3) скорость, м/сек	4) давление, am	6) заряд A T=1690°	7) заряд C T=2550°	
9) NH_4ClO_4 — 65% Полиэфир — 35%	50	20	2,9	3,0	2,6
	50	100	7,5	7,2	4,7
	100	20	3,8	3,9	2,6
	100	100	10,3	10,2	4.7
10) NH_4ClO_4 — 75% Полиэфир + эпоксидная смола — 25%	50	100	19,0	9,5	8,5
	100	100	12,0	11,9	8,5
	225	20	6,0	6,3	5,1

1) Propellant; 2) gas-flow characteristics; 3) velocity, m/sec; 4) pressure, atm; 5) erosional rate of combustion, mm/sec; 6) charge A, T = 1690°; 7) charge C, T = 2550°; 8) rate of combustion from face, mm/sec; 9) 35% polyester; 10) 25% polyester + epoxy resin.
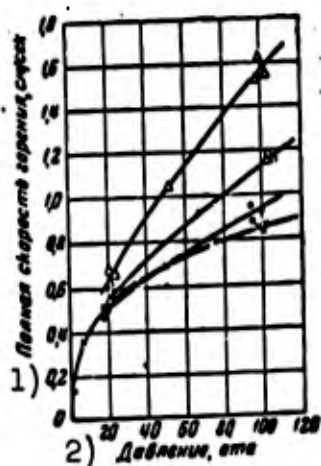
Fig. 222. Combustion rate of solid propellant as a function of conditions. x) facial combustion (average values); ●) erosional combustion, gas velocity 54 m/sec; 0) same, gas velocity 113 m/sec; Δ) same, velocity 236 m/sec. 1) Over-all combustion rate, cm/sec; 2) pressure, atm abs.

bustion rates of the solid propellants were studied. In erosional combustion, the propellant surface is acted upon not only by the heat flow from the flame front, but also by a gas flow moving over the material's surface. The case of erosional combustion occurs when solid propellants are burned from a central channel. The properties of the propellants tested are listed in Table 172 and the test results in Table 173.

Thus, the combustion rate of a solid propellant depends on the velocity of the gas flow moving over the surface of the propellant. The rate of erosional combustion is higher than that of combustion from the face.

This relationship is shown in Fig. 222.

The use of solid propellants in ramjet air-breathing engines represents a comparatively new field of application for them. Such fuels contain a large excess of combustible ($\alpha \sim 0.2$-0.25) and a small quantity of oxidizer — about 25% — to support combustion. The propellant charge is placed in the combustion chamber of a supersonic aircraft and burns in the air stream during combustion of the combustible excess. Solid fuels for ramjet air-breathing engines have the following compositions and characteristics:

Composition of Propellant, %		Characteristics	
Potassium nitrate	25	Density	1.65
Copper sulfate	10	Heating value	4450 kcal/kg
Aluminum	65	Combustion rate	13 mm/sec

Potassium nitrate	21.5	Density	1.25
Copper sulfate	8.5	Heating value	4800 kcal/kg
Magnesium	30	Combustion rate	32 mm/sec
Aluminum	25		
Boron	10		
Sulfur	5		

Potassium nitrate	25	Density	1.33
Copper sulfate	10	Heating value	5300 kcal/kg
Boron	20		
Aluminum	45		

Carbon	45	Density	1.45
Aluminum	20	Heating value	6600 kcal/kg
Boron	5		
Potassium nitrate	10		
Nitrocellulose	20		

Copper sulfate is added to these compositions as a combustion catalyst to raise the combustion rate. The combustion rate of the propellants at atmospheric pressure is 15-30 mm/sec [4].

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Manu-script Page No.	[Footnotes]
601	*Nitropolyvinyl alcohol $[-CH_2-CH(ONO_2)-]_x$ and nitropoly-styrene [17b] are recommended for these purposes.
610	*In this case, we imply operation of the engine at high altitudes above 100 km, where the density of the atmos-phere is negligibly small.
613	*Polyvinyl nitrate, nitropolystyrene with nitrotoluene additives and aluminum were recommended in 1960 as binders with ammonium perchlorate [17b].

Manu-script Page No.	[List of Transliterated Symbols]
529	обр= obr = obrazovaniye = formation

OXIDIZERS USED IN PROPELLANTS
FOR LIQUID REACTION ENGINES

INTRODUCTION

The oxidizer of a propellant for liquid reaction engines is that substance which is used, in its capacity as a propellant (fuel) component to accomplish the oxidation of the combustible in the ZhRD chamber. The properties of a ZhRD propellant are determined in great measure by the nature of the oxidizer, since the oxidizers used may differ markedly from one another in terms of properties, whereas organic combustibles show no such great divergence with respect to properties [1].

For example, propellants containing liquid oxygen as the oxidizer differ markedly from nitric-acid- and nitrogen-oxide-based propellants. Liquid oxygen has a boiling point of -183°. At this temperature it is extremely volatile and neutral in character. Nitric acid is used at temperatures that are almost 200° higher. Nitric acid boils at $+86^{o}$ and is a powerful acid.

Concentrated hydrogen peroxide also differs markedly in terms of properties from the first two oxidizers. One of the characteristic properties of hydrogen peroxide is its capacity to catalytic decomposition which takes place in the presence of fast catalysts which result in the liberation of a substantial quantity of heat.

We know of oxidizers which differ even more markedly in terms of properties from the first three; for example, fluorine and the oxides based on fluorine compounds.

The divergence in oxidizer properties has an effect on the nature

of the propellant. Propellants based on liquid oxygen, nitric acid, and hydrogen peroxide differ substantially in terms of energy and operational characteristics, although the combustibles (included in the composition of these propellants) may be of the same type (petroleum products) or may be quite close in terms of properties [9].

In connection with the above, particular attention must be devoted to propellant oxidizers in the propellant system for ZhRD.

Certain oxidizers for reaction [rocket] propellants can be divided into the following groups [1-3, 19, 20].

1) Nitric acid, nitric acid with oxides of nitrogen, and tetranitromethane. In the USA, 97-99% nitric acid is used as an oxidizer and identified by the conventional designation WFNA (MPD-579); the nitric acid containing 15-20% nitrogen oxides is designated as RFNA (MPD-25508).

Reference should also be made to a mixture of nitrogen oxides employed as oxidizers: $NO-N_2O_3-N_2O_4$ and tetranitromethane $C(NO_2)_4$ with 20-30% N_2O_4.

Ammonium nitrate NH_4NO_3 is used in solid propellants.

2) Liquid oxygen and solutions of ozone in liquid oxygen. Liquid oxygen was the first oxidizer which found practical application in rocket engineering and serves as one of the basic oxidizers at the present time. In recent years, a great study has been conducted in connection with ozone, as a result of which scientists in the USA have come to the conclusion that a 20-25% solution of ozone in liquid oxygen can be employed as an oxidizer in rocket engineering, in view of its greater efficiency as compared to that of oxygen alone.

3) Liquid fluorine. In recent years, this oxidizer has been used by the USA in rocket engines. In terms of efficiency, liquid fluorine as an oxidizer exhibits substantially better characteristics than does

- 636 -

liquid oxygen; however, the application of this oxidizer is being delayed by the difficulties encountered in storing it (liquid fluorine boils at -188.3°), as well as by the difficulties encountered in the transportation of the liquid fluorine, and the operation of engines using this oxidizer.

4) Compounds containing active fluorine. Among these, we should devote some attention to the oxygen compounds of fluorine F_2O, FNO_2, the halides of fluorine ClF_3, BrF_5, and recently derived compounds of fluorine — tetrafluorohydrazine N_2F_4 and perchlorylfluoride $FClO_3$, which are already being produced on an industrial scale in the USA.

Fluorine compounds, although their heating yield is smaller than that of fluorine in propellant mixtures, they are either liquid or have a higher boiling point than fluorine and can be used in liquid form or in the form of solutions in other liquid oxidizers at standard temperatures.

5) Perchloric acid $HClO_4$ in the form of its derivatives. Perchloric acid is a compound that exhibits limited stability but can be suggested for utilization in the form of 8-12% solutions in nitric acid, where it is found in the form of nitronium perchlorate NO_2ClO_4.

Another compound — anhydrous perchloryl fluoride, a completely stable compound, is suggested as an oxidizer in the USA.

Ammonium perchlorate NH_4ClO_4 is the basic oxidizer for solid rocket propellants.

6) Concentrated hydrogen peroxide — 80-90% H_2O_2. At the present time, this is used primarily as an auxiliary monocomponent propellant to actuate rocket turbopumps; we also know of its utilization in starter engines for aircraft, and there has been some indication of the possibility of using hydrogen peroxide in aviation ZhRD.

Of the above-enumerated oxidizers, some are being investigated,

and the utilization of others is still a matter of some doubt.

Liquid oxygen, nitric acid, and nitrogen oxides, as well as con-
centrated hydrogen peroxide have found practical application; liquid
fluorine is being tested on an industrial scale.

In the subsequent sections, individual properties of ZhRD oxidiz-
ers are examined.

Chapter 1

NITRIC ACID, NITROGEN OXIDES, TETRANITROMETHANE

Generally 98-99% nitric acid is used as the oxidizer for rocket propellants; this oxidizer, in foreign literature, is referred to as "white fuming nitric acid." The nitric acid contains varying quantities of nitrogen tetroxide. It has been proposed to use systems consisting of nitrogen oxide as oxidizers. For example, there have been reports on tests of oxidizers consisting of tetranitromethane and nitrogen tetroxide. The physicochemical properties of oxidizers based on nitric acid, nitrogen oxides, and tetranitromethane are presented in Table 174.

TABLE 174

Physicochemical Properties of Oxidizers Based on
Oxygen Compounds of Nitrogen [1, 2]

1 Окислитель	2 Мол. вес	3 Плотность	4 Т. пл., °C	5 Т. кип., °C	6 Теплота образования, ккал/моль	7 Теплопроизводительность с толуолом, ккал/кг
8 Азотная кислота	63,02	1,51 (20°)	— 41,6	86	41,40	1470
9 Четырехокись азота	92,02	1,45 (20°)	— 11,20	21,15	— 3,08	1790
10 Пятиокись »	108	1,63 (18°)	— 30	47	0,6	1830
11 Трехокись »	62	1,447 (2°)	—102	+ 4	20,0	—
12 Окись . »	30	1,27 (ж)	—164·	—151	—21,5	1610
13 Закись »	44	1,23 (ж, —8°)	—102,4	— 89,5	—19,5	1310
14 Тетранитрометан ...	196,04	1,64 (20°)	+ 13,8	126,0	— 8,9	1760

1) Oxidizer; 2) molecular weight; 3) density; 4) melting point, °C; 5) boiling point, °C; 6) heat of formation, kcal/mole; 7) heating yield with toluene, kcal/kg; 8) nitric acid; 9) nitrogen tetroxide; 10) nitrogen pentoxide; 11) nitrogen trioxide; 12) nitrogen oxide; 13) nitrous oxide; 14) tetranitromethane.

1. Nitric Acid

Nitric acid (100%) is unstable and decomposes quite rapidly at room temperature in accordance with the following equation:

$$2HNO_3 \rightleftarrows N_2O_5 + H_2O$$
$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$
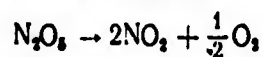
to 98-99% nitric acid, after which the decomposition process is sharply retarded by the water is formed in the reaction.

Since gaseous oxygen is liberated in the decomposition, extremely high pressures may develop in a closed volume. The magnitude of this pressure is a function of the volumetric ratio between the vapor (V_1) and liquid (V) phases. The rate of decomposition for concentrated nitric acid at 76° is shown in Fig. 223. At 76° and a volume of about 11% for the vapor phase, the pressure after a period of 16 hours may attain 90 atm [3].
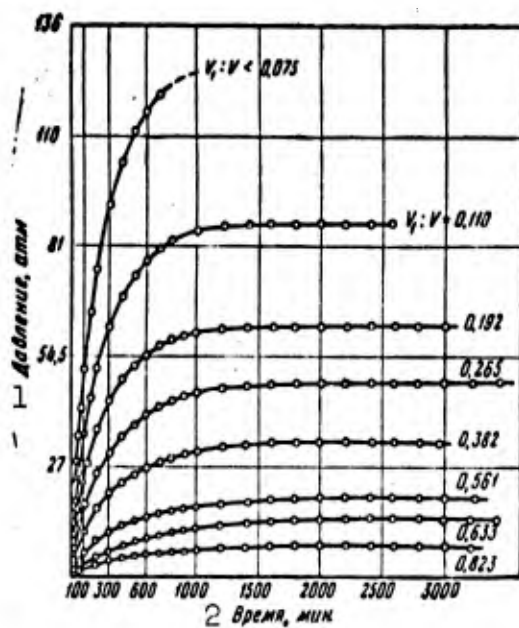
Fig. 223. Rate of decomposition for concentrated nitric acid at 76° and for various volumetric ratios between the vapor phase and the volume of the liquid phase $(V_1:V)$. 1) Pressure, atm; 2) time, min.

TABLE 175

Standard Thermodynamic Quantities (298, 16°K, and
1 atm) for Liquid and Gaseous Nitric Acid [4]

1 Кислота	2 ΔH кал/г·моль	3 ΔZ, кал/г·моль	ΔS	S	4 λисп, кал/г·моль	5 Pпл, кал/г·моль
6 HNO₃(ж)	−41349	−10032	−74,85	37,19	9355	2503
7 HNO₃(г)	−31904	−17556	−48,42	63,62	—	—

1) Acid; 2) ΔH, cal/g-mole; 3) ΔZ, cal/g-mole: 4)
λ_{isp}, cal/g-mole; 5) ρ_{pl}, cal/g-mole; 6) HNO₃
(liquid); 7) HNO₃ (gas).

The change in the density of nitric acid ranging from 90 to 100%
at 20° is presented below [3]:

Concentration, %	Density	Concentration, %	Density
100	1.5129	95	1.4932
99	1.5059	94	1.4912
98	1.5008	93	1.4892
97	1.4974	92	1.4873
96	1.4952	90	1.4826

The vapor tension of 98% nitric acid at 20 and 40°, respectively,
is 37 and 116.5 mm Hg.

The melting point of 100% nitric acid is equal to −41.6°; 98%
nitric acid, −42.3°; 94.9% nitric acid, −49.7°; and 90% nitric acid,
−68.5°. The diagram of state for the HNO₃-H₂O system is presented in
Fig. 224. The heat capacity of 98% nitric acid is equal to 0.475
kcal/mole·deg. The heat of formation of 100% nitric acid is 42.4
kcal/mole, and for 97.5% nitric acid it is 48.90 kcal/mole.

K.P. Mishchenko and A.A. Ravdel' [4] present the thermodynamic
characteristics for nitric acid (Table 175).

Nitrogen tetroxide dissolves well in nitric acid. With the solu-
tion of N_2O_4 in HNO_3, the solidification point is reduced for the mix-
ture whereas its specific weight is increased, and this can be seen
from the following data [5]:

Composition of solution, %		Solidification point, °C
HNO$_3$	N$_2$O$_4$	
100	–	–42
96.6	3.4	–58.5
85	15	–70
82	18	–73
70	30	–58.5
66	34	–48.5

The solution of nitrogen tetroxide in nitric acid makes it possible to obtain an oxidizer with a low solidification point (below –60°).
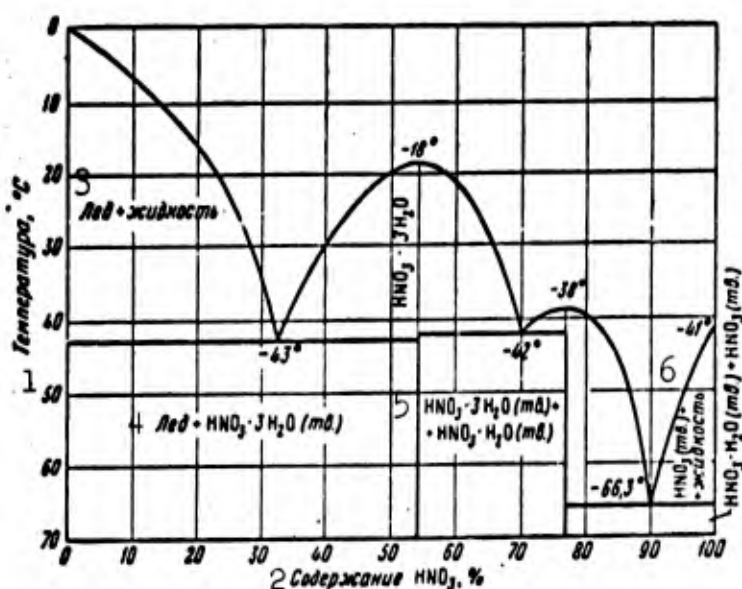
Fig. 224. Diagram of state for the HNO$_3$-H$_2$O system. 1) Temperature, °C; 2) content of HNO$_3$, %; 3) ice + liquid; 4) ice + HNO$_3$ x x 3H$_2$O (solid); 5) HNO$_3$·3H$_2$O (solid) + + HNO$_3$·H$_2$O (solid); 6) HNO$_3$ (solid) + liquid.

Solutions of nitrogen tetroxide in anhydrous nitric acid are denser than both the initial acid and the nitrogen oxides (Table 176).

This relationship is also presented in Fig. 225.

The nitric acid-nitrogen tetroxide system was the subject of a number of investigations [7, 8].

The technical requirements for concentrated nitric acid and melange are presented in Table 177.

TABLE 176

Density of Solutions of Nitrogen Tetroxide in Nitric Acid at 25° [6]

1 Содержа- ние N_2O_4, %	2 Плотность	3 Содержание N_2O_4, %	4 Плотность
0	1,5018	14	1,5606
2	1,5105	16	1,5683
4	1,5193	18	1,5760
6	1,5227	20	1,5838
8	1,5361	26,5	1,5927 } (23°)
10	1,5433	36,0	1,610
12	1,5525		

1) Content of N_2O_4, %; 2) density; 3) content of N_2O_4, %; 4) density.
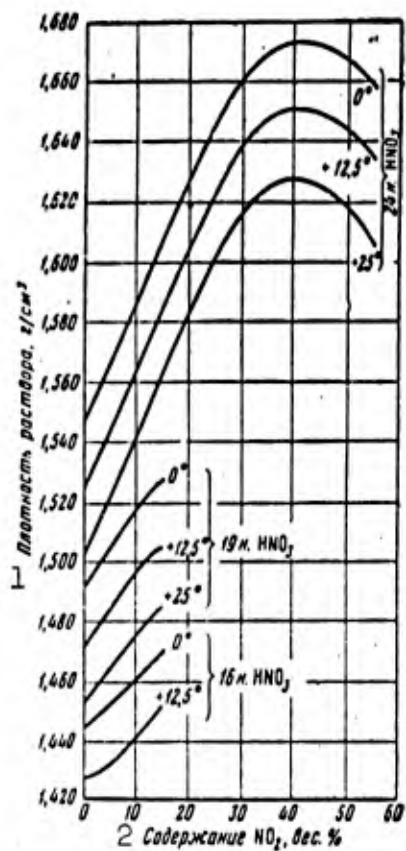
Fig. 225. Density of solutions of N_2O_4 in HNO_3 as a function of composition. 1) Density of solution, g/cm^3; 2) content of NO_2, % by weight.

TABLE 177

Technical Requirements with Respect
to Concentrated Nitric Acid and
Melange [Mixture]

1 Показатели	2 Азотная кислота		5 Меланж первого сорта
	первый сорт 3	второй сорт 4	
6 Концентрация азотной кислоты (%), не менее	98	96	89,0
7 Содержание окислов азота (%), не более	0,3	0,4	0,4
8 Содержание серной кислоты (%), не более.	0,1	0,2	7,5
9 Содержание твердого остатка (%), не более.	0,05	0,07	0,12
10 Содержание воды (%), не более	—	—	3,0

1) Indicators; 2) nitric acid; 3)
first kind; 4) second kind; 5) me-
lange of first kind; 6) nitric-acid
concentration (%), no less than; 7)
nitrogen-oxides content (%), no more
than; 8) sulfuric-acid content (%),
no more than; 9) solid-residue con-
tent (%), no more than; 10) water
content (%), no more than.

Nitric acid (98%) with nitrogen oxides have found practical ap-

plication as oxidizers. Melange was used as an oxidizer in Germany.

The corrosion produced by concentrated nitric acid in the liquid

phase and in the vapor phase is of great significance in selecting the

material from which the rocket equipment is to be fabricated.

Table 178 presents data on the corrosion activity of concentrated

nitric acid containing 6.5 and 16% nitrogen tetroxide and 12% sulfuric

acid (melange), with respect to the various types of steels at tem-

peratures ranging from $+10^{\circ}$ to $+27^{\circ}$.

With respect to conventional steel, nitric acid exhibits pronounced

corrosive properties.

Only chrome-nickel steels and high-silicon iron are stable with

respect to concentrated nitric acid.

Aluminum and steels of brands Kh17, Kh25, and Kh18N9 (in accord-

ance with the classification system adopted in the USSR) are stable to nitric acid.

In addition to corrosion, a tremendous deposit of mineral salts is accumulated at the bottom of the cavity as a result of corrosion. Initially soft and jelly-like, this deposit eventually converts into solid grains.

Temperature has a significant effect on corrosion. The effect of temperature on corrosion is presented in Table 179.

TABLE 178

Magnitude of Metal Corrosion in Nitric Acid (mm/year) [9]

1 Материал	2 Концентрированная азотная кислота			6 Примечание	
	с 6,5% N_2O_4 3	с 16% N_2O_4 4	с 12% H_2SO_4 5		
7 Литое железо	12,7	10,1	—	Не устойчиво	10
8 Сталь SAE-1020 . .	0,25	0,76	0,025	Относительно устойчи- ва	11
9 Нержавеющая сталь AISI-304	0,010	0,010	0,015	Вполне устойчива	12

1) Material; 2) concentrated nitric acid; 3) with 6.5% N_2O_4; 4) with 16% N_2O_4; 5) with 12% H_2SO_4; 6) remarks; 7) cast iron; 8) SAE-1020 steel; 9) AISI-304 stainless steel; 10) not stable; 11) relatively stable; 12) completely stable.

TABLE 179

Effect of Temperature* on the Corrosion of Stainless Steel through the Action of Concentrated Nitric Acid with 6.5% N_2O_4 [9, 10]

1 Температура, °C	2 Величина коррозии, мм/год	1 Температура, °C	2 Величина коррозии, мм/год
27	0,010	97	7,620
54	0,178	110	12,700
80	5,080	120	30,500

*The assignments were carried out under pressure at temperatures above the boiling point of nitric acid.

1) Temperature, °C; 2) magnitude of corrosion, mm/year.

Effect of Addition of Sulfuric
and Orthophosphoric Acids on the
Corrosion of SAE-1020 Steel
through the Action of Concen-
trated Nitric Acid with 16% Nit-
rogen Tetroxide [9, 10]

1 Содержание добавки, %	2 Величина коррозии азотной кислотой (мм/год) с добавками	
	H₂SO₄	H₃PO₄
0,0	0,279	0,279
1,0	0,051	0,030
2,0	0,025	0,102
4,0	0,015	0.708

1) Content of admixture, %; 2)
magnitude of corrosion (mm/year)
with nitric acid and admixtures.

The corrosion due to nitric acid can be reduced through the addi-
tion of sulfuric (98%) or orthophosphoric acid (85%) to the nitric
acid (Table 180).

The sulfuric acid reduces the corrosion produced by the nitric
acid. The phosphoric acid reduces corrosion only in the case of admix-
tures in a quantity up to 1.0%, after which corrosion again increases.

Prior to 1951, 98% nitric acid was used in rocket engineering in
the USA; it was used particularly for the anti-aircraft defense rocket
"Nike." In 1952, nitric acid was replaced by a nitric acid containing
20-25% nitrogen oxides. This is associated with the fact that the nit-
ric acid decomposes, liberating oxygen, when stored in hermetically
sealed rocket tanks; in this case, the oxygen creates pressure of sev-
eral tens of atmospheres, leading to the bursting of the membrane sep-
arating the tank and the engine. Nitric acid containing 20-30% nitro-
gen oxides is stable in storage and does not liberate oxygen, and has
less of a corrosive effect on the aluminum tanks.

An investigation carried out by the Jet Propulsion Laboratory of
the California Institute of Technology demonstrated that the addition

of a small quantity of hydrogen fluoride (a fraction of a percent) to nitric acid substantially reduces the corrosive action against aluminum and stainless steel as a result of the formation of a protective fluoride film on the surface of the metal.

Nitric acid containing a small quantity of water and nitrogen oxides is also recommended as a stable oxidizer having the following composition: 98% nitric acid, 100 parts by weight; N_2O_4, 2-4 parts by weight; and H_2O, 2-4 parts by weight.

Nitric acid is an oxidizer that is available on a large industrial scale. For example, the production of nitric acid in the USA during the past 10 years was as follows [11]:

	million tons annually
1951..................................	1.5
1956..................................	2.6
1957..................................	2.8
1960..................................about	4.0

The cost of nitric acid is comparatively low in comparison with other oxidizers. For example, according to 1957 data, the cost in the USA per ton of oxidizer was as follows:

Liquid oxygen.........................	110 dollars
Nitric acid (98%)......................	220 dollars
Nitric acid (78%) Nitrogen oxides (22%)	240 dollars
Tetranitromethane......................	660 dollars

2. Nitrogen Oxides

In addition to nitric acid, nitrogen tetroxide (N_2O_4) may also be employed as a component in rocket propellants.

Nitrogen tetroxide under normal conditions is not an individual substance, but represents a mixture of two equivalent forms:

$$N_2O_4 \rightleftarrows 2NO_2$$
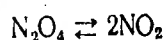
Technical nitrogen tetroxide contains no more than 0.1% of water. Moist nitrogen tetroxide corrodes conventional steels. However, when dry N_2O_4 (or with a moisture content not exceeding 0.1%) has virtually no effect on steel. Therefore N_2O_4 is stored and transported in conventional steel low-pressure flasks. At 35°, the vapor pressure of N_2O_4 amounts only to 2 atm [11].

Nitrogen tetroxide, as well as other oxides (NO and N_2O_3) are toxic.

Under laboratory conditions, nitrogen tetroxide can be derived from the following reaction:

$$3NaNO_2 + 2HNO_3 \rightarrow 3NaNO_3 + 2NO + H_2O$$
$$NO + 2HNO_3 \rightarrow 1^1/_2N_2O_4 + H_2O$$
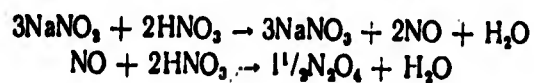
Industrially, nitrogen tetroxide is obtained by the two-stage oxidation of ammonia: initially nitric oxide is obtained, and this is then oxidized into the tetroxide.

A system of nitrogen oxides $NO-N_2O_4$ has been reported [12, 13], and this system consists of a mixture of equivalent quantities of three oxides:

$$xNO \rightleftarrows yN_2O_3 \rightleftarrows zN_2O_4$$
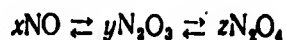
N_2O_3 is formed as a result of the reduction of nitrogen tetroxide with nitric acid:

$$2NO + N_2O_4 \rightleftarrows 2N_2O_3$$
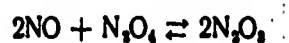
This system can also be of interest from the standpoint as serving as an oxidizer for rocket propellants.

Nitrogen trioxide is a compound which is stable and decomposes easily at standard temperature. However, under some pressure in a mixture of equivalent quantities of other nitrogen oxides (NO and N_2O_4) nitrogen trioxide is quite stable.

The ternary system $NO-N_2O_3-N_2O_4$, obtained by the solution of NO
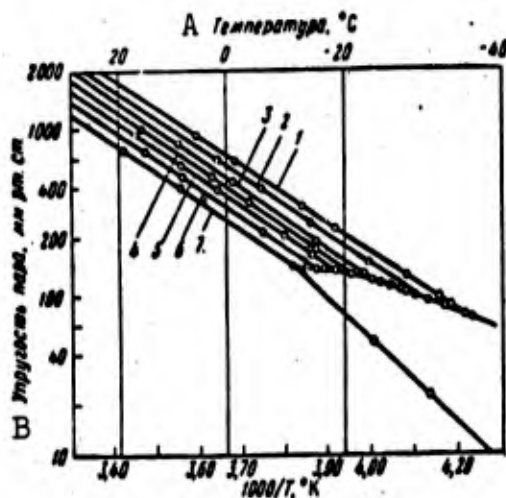
Fig. 226. Vapor pressure above the
$NO-N_2O_4$ system as a function of tem-
perature. 1) 16.85% NO; 2) 14.11%
NO; 3) 10.67% NO; 4) 8.30% NO; 5)
5.55% NO; 6) 2.89% NO; 7) N_2O_4. A)
Temperature, $^{\circ}C$; B) vapor pressure,
mm Hg.

in N_2O_4, has the following points of solidification as a function of

the content of NO in N_2O_4:

Content of NO, %	M.p., $^{\circ}C$
0	—11,3
2,89	—14,1
5,55	—17,06
8,30	—20,4
10,67	—23,51
14,11	—28,81
16,85	—33,61
20	—40

The vapor pressure for a 16.85% solution of NO can be presented

by the following equation:

$$\log p = 9.0347 - 1702 \cdot 1/T \text{ mm Hg.}$$

Figure 226 shows the vapor pressure above the $NO-N_2O_4$ system. The

diagram of state for the $NO-N_2O_3-N_2O_4$ or $N_2O_3-N_2O_4$ systems are pre-

sented in Fig. 227.

In the USA, handbook oxidizer tables point to an oxidizer the fol-

lowing composition: N_2O_4, 70%; and NO, 30%, i.e., a $NO-N_2O_3-N_2O_4$ system.

- 649 -

This oxidizer with triethylamine yields a specific impulse that is 10 units higher than nitric acid with the same combustible.
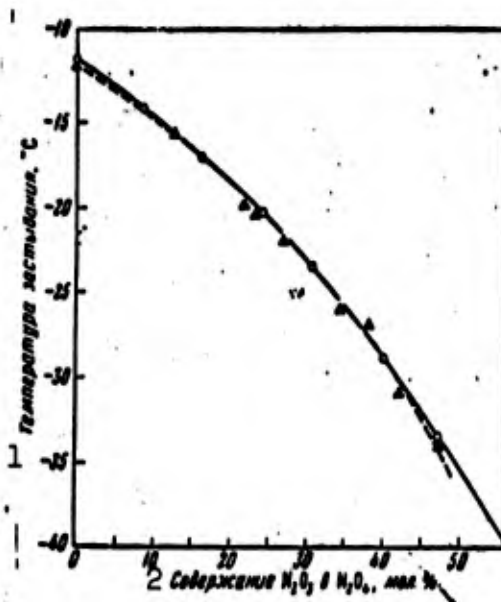
Fig. 227. Solidification point of the $N_2O_3-N_2O_4$ system. 1) Solidification point, ^oC; 2) content of N_2O_3 in N_2O_4, % mol.

3. Tetranitromethane

Tetranitromethane has been known as an oxidizer for several tens of years and was long ago suggested for the preparation of explosive mixtures [14].

Subsequently, tetranitromethane was proposed as an oxidizer for rocket propellants. However, the physicochemical properties of tetranitromethane make it impossible to use it directly as an oxidizer. For example, the melting point of tetranitromethane ($+14.2^o$) prevents its utilization under all operating conditions. On the other hand, this oxidizer exhibits substantial advantages over nitric acid. It exhibits a high specific weight of 1.643 at 20°, a boiling point of 126°, and in a vapor with combustibles forms a propellant with a high heating yield (1760 kcal/kg). Tetranitromethane is a weak endothermic compound whose heat of formation is 8.96 kcal/mole [15].

The heat of tetranitromethane decomposition is quite substantial and amounts to 102.9 kcal/g-mole or 526 kcal/kg. It is for this reason that tetranitromethane exhibits such poor explosive properties.

Tetranitromethane has been proposed for use in a mixture with nitrogen oxides in the following relationship: $C(NO_2)_4$, 70% and N_2O_4, 30% [16]. This solution has a low solidification point of $-30°$ and is virtually explosion-proof.

Tetranitromethane can be obtained in a variety of ways, as for example:

1) by the nitration of trinitromethane with nitric acid;

2) by the destructive nitration of aromatic hydrocarbons with nitric acid;

3) by the destructive nitration of aromatic nitro derivatives with nitric acid;

4) by the nitration of acetic anhydride with nitric acid;

5) by the nitration of ketene with nitric acid.

During the First World War, the production of tetranitromethane was accomplished by the nitration of acetic anhydride with nitric acid:

$$4\,(CH_3CO)_2O + 4HNO_3 \rightarrow C(NO_2)_4 + 7CH_3COOH + CO_2.$$
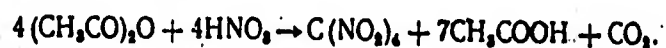
In order to employ this method to produce tetranitromethane in a laboratory, 126 g concentrated nitric acid is introduced slowly into a flask containing 205 g acetic anhydride, cooled to $-5°$. After a period of 3 hours, the mixture is kept at $0°$, and then kept 8 days at room temperature, after which it is heated for 1 hour to $45-50°$. Then the mixture is poured into a glass vessel containing water, where 10 g tetranitromethane settles out, and this represents a yield of 72%.

This method is associated with a tremendous consumption of acetic anhydride and nitric acid.

A better method is the one that is based on the nitration of

acetylene with nitric acid. This reaction can be presented by the following summary equation [17]:

$$5HC \equiv CH + 38HNO_3 \rightarrow 3\,C(NO_2)_4 + 7CO_2 + 26NO_2 + 24H_2O$$

A convenient method for the derivation of tetranitromethane is the reaction of the nitration of ketene with 98-99% nitric acid in accordance with the following reaction [18]:

$$4CH_2 = C = O + 4HNO_3 \rightarrow C(NO_2)_4 + CO_2 + 3CH_3COOH$$
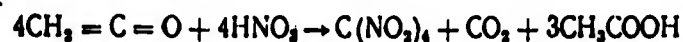
In diluting the reaction mass with water, up to 90% of the tetranitromethane is isolated. During the nitration, the ketene bubbles through the layer of nitric acid if well cooled with ice. The ketene is obtained by the pyrolysis of acetone

$$CH_3 - CO - CH_3 \rightarrow CH_2 = C = O + CH_4$$
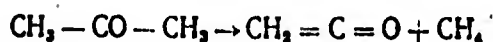
The initial substance for the derivation of acetone is propylene from cracking gases.

The nitration of acetylene, in order to produce tetranitromethane, has been studied in great detail. This method was checked on continuous-action experimental installations. For example, it was possible to obtain 10 kg of tetranitromethane on this continuous-action laboratory installation. A diagram of this installation is presented in Fig. 228.

The nitration of acetylene with nitric acid is carried out in three series-connected columns 1, 2, and 3. The total capacity of these columns amounts to approximately 3 liters. The first two columns are filled with 98% nitric acid in a mixture with regenerated nitric acid containing about 0.14 g mercury nitrate per 1 liter of nitric acid. The mercury nitrate is the catalyst in the nitration reaction. Within 1 hour 2.4 liters of the nitration mixture is introduced into the upper part of the column and 93.5 liters of acetylene are introduced into the lower part of the first column in an hour through a special distribution device which provides for the good mixing of the reagents.

The nitration reaction in the first two columns is carried out at a temperature of 50-55° as a result of which the trinitromethane is formed.

The continued reaction of the nitration of trinitromethane in tetranitromethane is carried out in the third column. This reaction is carried out at 90° in the presence of 95% sulfuric acid. A solution of trinitromethane in nitric acid enters this column continuously in addition to the 1.7 liters/hour of sulfuric acid. The heating of the reaction column is carried out by means of a steam jacket. The reaction mixture entering into the separator 4 from column 3 is separated into two layers: the upper layer consists of crude tetranitromethane, and the lower layer consists of a mixture of waste acids. The crude tetranitromethane enters the lower part of the flushing column 5 into whose upper part there is a constant flow of concentrated sulfuric acid. The tetranitromethane, on passing through the layer of sulfuric acid, is flushed free of admixtures and accumulates in the upper part of the column from which it enters the purified-tetranitromethane collector 6.

The waste-acid mixture, after separation in the separator 4, is pumped into the rectification column 7 where the nitrogen oxides and nitric acid is boiled off. The final separation of the nitric acid from the sulfuric acid is carried out in a still 8, where the sulfuric acid is also made stronger. Increased to a concentration of 95-96%, the sulfuric acid enters the collector 9 and is again used in the process.

In the concentrated nitric acid obtained in the distillation in column 7 there are oxides of nitrogen and an admixture of tetranitromethane. This acid is employed for the preparation of the nitrating mixture by the addition of fresh nitric acid and the required quantity of mercury nitrate.
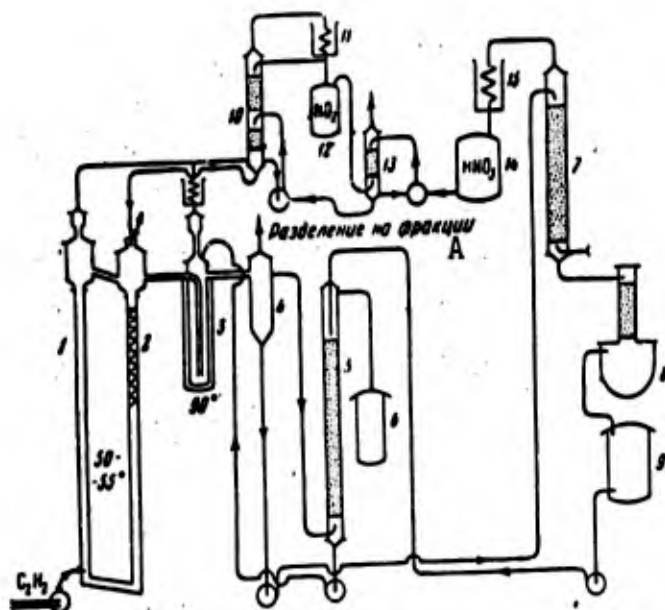
Fig. 228. Continuous-action laboratory installation for nitration of acetylene with nitric acid. 1 and 2) Columns for the nitration of acetylene with nitric acid; 3) column for the nitration of trinitromethane with a mixture of sulfuric and nitric acid; 4) separator for the separation of crude tetranitromethane; 5) column for the flushing of the crude tetranitromethane; 6) purified-tetranitromethane collector; 7) rectification column for separation of concentrated nitric acid; 8) still for concentration of sulfuric acid; 9) sulfuric-acid collector; 10) scrubber for flushing of waste gases; 11) condenser; 12) collector for regenerated nitrogen oxides; 13) cold-flushing scrubber; 14) nitric-acid collector; 15) condenser. A) Separation into fractions.

With the nitration of the acetylene from the first column, carbon dioxide and nitrogen dioxide are liberated. These gases are passed through scrubber 10 in which they are flushed with hot concentrated nitric acid containing mercury nitrate in order to remove the traces of acetylene. After flushing the nitric acid is passed on to carry out the first stage of the nitration process. The gases from the scrubber are passed through a deep-cooling coil where the nitrogen dioxide is condensed.

The resultant nitrogen dioxide is used for the preparation of nitric acid.

The incompressible part of the waste gases is passed through scrubber 13 in which the gases are flushed with cold concentrated nitric acid and where the nitrogen oxides are finally absorbed. The utilization of a closed extraction and regeneration system reduces losses of tetranitromethane and nitrogen dioxide.

The installation has a capacity of 440 g of purified tetranitromethane per hour. The tetranitromethane yield, with this process, amounts to 60% of the theoretical yield.

The chemical mechanism of the reactions taking place in the derivation of tetranitromethane can be presented as proceeding in the following stages:

1) in the first stage, during the reaction between the acetylene with nitric acid, dinitro-, and then trinitroacetaldehyde are formed:

$$HC \equiv CH + 2HNO_3 \rightarrow (NO_2)_2CH - CHO + H_2O$$
$$(NO_2)_2CH - CHO + HNO_3 \rightarrow (NO_2)_3C - CHO + H_2O$$
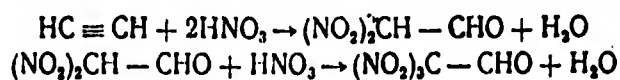
2) the oxidation of the trinitroacetaldehyde into trinitroacetic acid, with its subsequent decomposition, and the formation of trinitromethane:

$$(NO_2)_3C - CHO + 2HNO_3 \rightarrow (NO_2)_3C - COOH + 2NO_2 + H_2O$$
$$(NO_2)_3C - COOH \rightarrow (NO_2)_3CH + CO_2$$
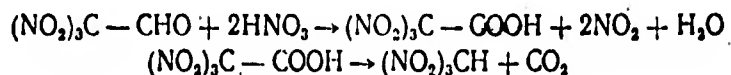
3) the nitration of trinitromethane into tetranitromethane. This reaction concludes in the presence of sulfuric acid at 90°:

$$(NO_2)_3CH + HNO_3 \rightarrow (NO_2)_4C + H_2O$$
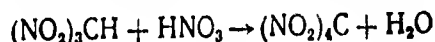
These reactions can be used to explain the formation of a great quantity of nitrogen oxides and carbon dioxide in the nitration of acetylene with nitric acid.

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Chapter 2

CONCENTRATED HYDROGEN PEROXIDE

Concentrated hydrogen peroxide (80-90%) is used abroad as a mono-propellant in starter aviation engines, but its primary use is as an auxiliary propellant (fuel) to actuate turbopump installations of ZhRD

TABLE 181

Physicochemical Properties of Hydrogen Peroxide [1]

1 Показатели	2 Концентрация перекиси водорода, %		
	80	90	100
3 Плотность	1,35 (15°)	1,39 (25°)	1,444 (18°)
4 Т. пл., °C	—22,2	—11,1	—1,7
5 Т. кип. (с разложением), °C . . .	—	140	151,4
6 Вязкость при 18°, сст	1;307 (15,5°)	1,30	1,307
7 Показател преломления n_D^{20} . .	—	1,308	1,4139
8 Теплота парообразования, ккал/кг	—	328	326
9 Поверхностное натяжение, дин/см	—	75,53	75,7
10 Теплота разложения, ккал/г-моль	—	—	23,450
11 Теплота образования, ккал/г-моль			
12 жидкая H_2O_2	—	—	45,16
13 парообразная H_2O_2	—	—	38,29
14 Теплоемкость, кал/г·град	0,64	0,58	0,57

1) Indicators; 2) concentration of hydrogen peroxide, %; 3) density; 4) melting point, °C; 5) boiling point (with decomposition), °C; 6) viscosity at 18°, centistokes; 7) refractory index n_D^{20}; 8) heat of vapor formation, kcal/kg; 9) surface tension, dyn/cm; 10) heat of decomposition, kcal/g-mole; 11) heat of formation, kcal/g-mole; 12) liquid H_2O_2; 13) gaseous H_2O_2; 14) heat capacity, cal/g·deg.

[liquid rocket (reaction) engines], and it is used in certain cases as an oxidizer for rocket propellants [1, 2].

The physicochemical properties of hydrogen peroxide, of various

concentrations, are presented in Table 181.

Figure 229 shows the diagram of state for the H_2O_2-H_2O system. With a drop in temperature, the solid phase settles out of 90-95% hydrogen peroxide. 90% H_2O_2 can be supercooled. By means of additional quantities of ammonium nitrate to 92% hydrogen peroxide, the melting point of the latter can be reduced from -9.1 to -32° (Fig. 230).

A mixture consisting approximately of 40% ammonium nitrate and 60% hydrogen peroxide has a lower solidification point. A solution of this type may be of interest from the standpoint of serving as an oxidizer for rocket propellants.

Hydrogen peroxide decomposes with substantial liberation of heat and can therefore serve as a convenient energy source:

H_2O_2 (liquid) $\rightarrow$ H_2O (liquid) + $1/2O_2$ + 23.45 kcal/mole or 691 kcal/kg

H_2O_2 (liquid) $\rightarrow$ H_2O (gas) + $1/2O_2$ + 12.850 kcal/mole or 378 kcal/kg

H_2O_2 (gas) $\rightarrow$ H_2O (gas) + $1/2O_2$ + 24.5 kcal/g-mole
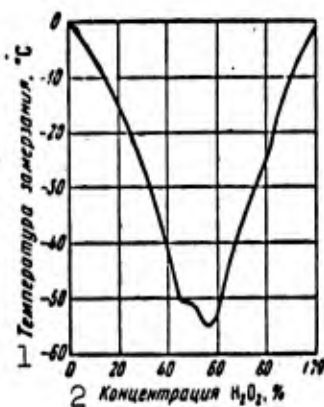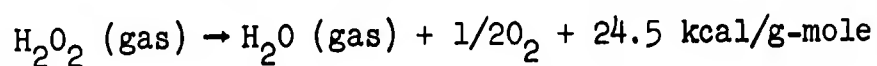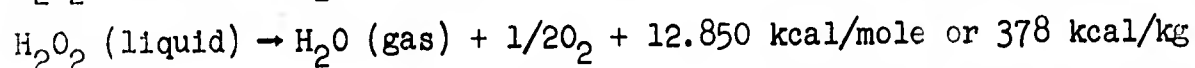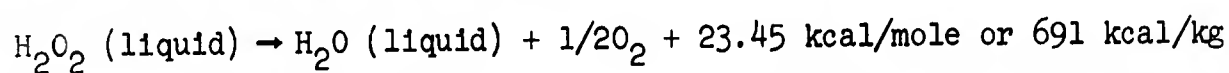
Fig. 229. Diagram of state of the H_2O_2-H_2O system. 1) Solidification point, ^{o}C; 2) concentration of H_2O_2, %.

The decomposition of hydrogen peroxide takes place in the presence of a fast catalyst. In the decomposition of 1 kg 90% hydrogen peroxide, 0.423 kg active oxygen is liberated as are 1700 liters of gas heated
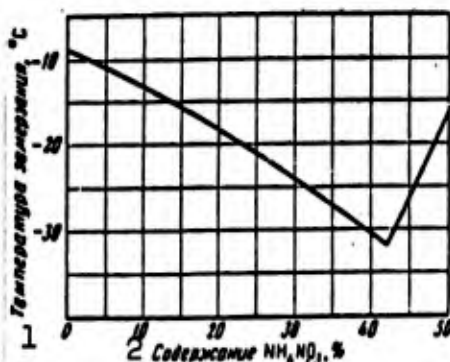
Fig. 230. Solidification point
for solutions of ammonium nit-
rate in hydrogen peroxide. 1)
Solidification point, ^{O}C; 2)
content of NH_4NO_3, %.

TABLE 182

Rate of Decomposition of 90%
Hydrogen Peroxide at Various
Temperatures [1, 2]

Температура, ^{O}C 1	Приближительная скорость разложения, 2
30	3 1% в год
66	4 1% в неделю
100	5 2% за 24 часа
140	6 Разлагается быстро

1) Temperature, ^{O}C; 2) approx-
imate decomposition rate; 3)
1% annually; 4) 1% weekly; 5)
2% daily; 6) decomposes quickly.

TABLE 183

Effect of Admixtures on Rate of
Decomposition of 90% Hydrogen
Peroxide at 100 [sic] in a 24-
Hour Period [1, 2]

Добавка 1	Количество добавки, мг/л 2	Потери первоначаль-но активного кисло-рода, % 3
4 Без добавок ...	—	2
5 Алюминий ...	10	2
6 Хром ...	0,1	96
7 Медь ...	0,1	85
8 Железо ...	1,0	15

1) Addition; 2) additional quantity, mg/liter; 3)
loss of initial active oxygen, %; 4) without addi-
tions; 5) aluminum; 6) chrome; 7) copper; 8) iron.

to 740°.

The slow decomposition of hydrogen peroxide occurs at normal temperatures. The rate of this process is a function of the presence of catalytic admixtures. For example, for a high-purity industrial specimen of 90% hydrogen peroxide, the rate of decomposition is expressed by the following quantities as a function of temperature (Table 182).

The most insignificant of admixtures will accelerate the decomposition of the hydrogen peroxide (Table 183).

The dust and dirt which may contaminate the product also promote the decomposition of hydrogen peroxide.

Acidic solutions of hydrogen peroxide are more stable with respect to decomposition than are neutral or alkaline solutions.

The addition of certain additives (stabilizers) to the hydrogen peroxide makes it possible to reduce the decomposition rate. Phosphoric and pyrophosphoric acids, their salts, boric acid, stannic, acetic, oxalic acids, as well as hydrooxyquinoline, acetanilide, etc., are used as stabilizers. The mechanism of stabilizer action involves their elimination or deactivation of the catalysts for the decomposition of the hydrogen peroxide.

The high purity of the hydrogen peroxide in combination with a stabilizer is the best guarantee of hydrogen-peroxide stability during storage. The stabilizers also guarantee the preservation of the hydrogen peroxide in the presence of various admixtures.

However, if the hydrogen peroxide is contaminated by large quantities of admixtures, no stabilizers can prevent the rapid decomposition of the product.

For the stabilization of H_2O_2 in storage, a small quantity of phosphoric acid is added; for example, 23 mg/liter is added for 87% hydrogen peroxide. The stabilizer quantity varies as a function of the

degree of product purity.

The greatest danger during storage exists when various contaminants, capable of producing the rapid catalytic decomposition of the H_2O_2, enter the space (volume) containing the hydrogen peroxide. In this case, the decomposition may be accelerated to such an extent that the safety valves will no longer function effectively. In this case, it is expedient to add an additional quantity of stabilizer — phosphoric acid — to the liquid H_2O_2. However, if this proves to be inadequate, then the concentrated hydrogen peroxide must be diluted to a 67% concentration at which it is no longer dangerous [1].

Concentrated hydrogen peroxide must be handled carefully, since if it comes in contact with combustibles or contaminant materials, spontaneous combustion is sometimes possible. If hydrogen peroxide comes into contact with the skin, serious burns are possible.

The best structural material for the storage of concentrated hydrogen peroxide is aluminum of high purity (99.6%). Aluminum containers must be thoroughly cleaned prior to being filled, and they must be flushed with a solution of caustic soda and then with water and 10% sulfuric acid of high purity for several hours. Then the acid is rinsed out with distilled water, after which it is desirable to rinse the container with hydrogen peroxide. On refilling, if the container has not become contaminated, the rinsing procedure is unnecessary [1, 2].

In this connection, large quantities of concentrated hydrogen peroxide are stored in aluminum barrels having a capacity of 100 to 120 kg. Aluminum tanks with a capacity of more than 15,000 liters are used for the transportation of this material, and these tanks are installed on railroad flatcars. The tanks have been fitted out with safety valves to handle excess pressure. In storage, losses of concentrated hydrogen peroxide should not exceed more than 1% annually [4].

Bottles of chemically stable glass with an external aluminum safety shield are used for the storage of concentrated hydrogen peroxide under laboratory conditions. Stainless-steel pumps may be used to pump hydrogen peroxide, and polyvinyl chloride is used for the packing [3, 5].

Teflon (polytetrafluoroethylene) and polyethylene, somewhat less, are stable to concentrated hydrogen peroxide.

Certain stainless steels, with properly treated surfaces, can withstand being in contact with hydrogen peroxide at 20° for intermittent periods over several days [5].

Copper, lead, and certain alloys cause the rapid intensive decomposition of hydrogen peroxide. For a comparatively short period of time concentrated hydrogen peroxide can be stored in tanks made of elastic plastics made of polyvinyl chloride and polyvinyl acetate. Hydrogen peroxide is drawn from these tanks under the action of external pressure which compresses the tanks [5].

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Chapter 3

LIQUID OXYGEN AND LIQUID OZONE

1. Oxygen

At the present time, liquid oxygen is in use abroad as an oxidant in fuels for long-range rockets. Its use as an oxidant for fuels in aviation liquid reaction-thrust engines has also been reported.

In industry, oxygen is widely used to intensify processes in the metallurgical and chemical industries, in oxyacetylene welding, to produce cheap commercial explosives (oxyliquits) and for other purposes [1].

Liquid oxygen is a transparent blue-tinted liquid with a specific gravity of 1.14. The boiling point of liquid oxygen is -183°, and its melting point is -219°. The critical temperature for oxygen is -118.8° and the critical pressure corresponding to this is 49.7 atm. The viscosity of liquid oxygen (96% concentration) at the boiling point is 0.189 centipoise, its latent heat of evaporation is 1.632 kcal/mole, and the heat capacity of oxygen in the range from -173 to $+25^\circ$ lies between 7.0 and 6.9 cal/mole. The heat expended on evaporation of the oxygen and heating of its vapors to $+18^\circ$ must be taken into account in calculations for the fuels. This quantity amounts to 3.1 kcal/mole.

Liquid oxygen is produced in industry by liquefying atmospheric air with alternating compression and cooling cycles, with the result that its temperature is lowered to -180°, at which the air condenses under relatively low pressure.

Apart from the other physicochemical properties, the compressibil-

ity of liquid oxygen is of great importance.

It has been shown by special experiments that the compressibility of a fuel may exert considerable influence on the performance stability of a liquid-fuel rocket engine and on the combustion completeness of the fuel; it is characterized by the compressibility coefficient, the magnitude of which is determined by the following expression:

$$K_t = \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \quad \text{isothermal compressibility}$$

$$K_a = \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_S \quad \text{adiabatic compressibility}$$

where $\underline{v}$ is the volume, $\underline{p}$ is the pressure, T is the temperature, and S is the entropy of the liquid.

The coefficients of adiabatic and isothermal compressibility are related as follows:

$$K_t - K_a = \frac{Tva^2}{C_p}.$$

The compressibility of liquid oxygen is very small, and the difference between the volumes of liquid oxygen at pressures of 1 and 70 atm does not exceed 1%.

Calculated values of the isothermal compressibility coefficient and other parameters of liquid oxygen are listed in Table 184.

A diagram of an apparatus for producing liquid oxygen with a low-pressure cold cycle and a compressed-gas engine appears in Fig. 231 [1]. Air is compressed to a pressure of 6-7 atmospheres in the turbocompressor 1, passes through the water cooler 2 and is then fed into the heat exchanger 3, where it is cooled to -160°; then almost all of the air (about 95% of the total quantity) enters the compressed-gas engine 4, where it expands to 1 atmosphere and, in the process, cools almost to the liquefication temperature. Emerging from the compressed-gas engine, the expanded air enters the tubing of the liquefier (condenser) 5, where it transfers its low temperature to the remaining 5%

TABLE 184

Theoretical Values of Isothermal Compressibility
Coefficient and Other Parameters of Liquid Oxygen

1 Температура, °C	2 Удельный вес	3 Удельный объем, см³/г	a	4 c_p, кал/г·град	5 Ta^2/c_p, см³/кал·10⁻³	6 K_1, см²/кг·10⁻⁶
—183	1,142	0,8757	4,21	0,4059	3,441	183
—188	1,167	0,8569	4,15	0,4039	3,106	165
—193	1,191	0,8396	4,03	0,4019	2,714	148
—198	1,215	0,8230	3,94	0,4008	2,390	132
—203	1,239	0,8071	3,82	0,3989	2,065	117,3
—208	1,263	0,7918	3,65	0,3972	1,726	102,5
—213	1,282	0,7800	3,46	0,3962	1,422	89,5

1) Temperature, ^{o}C; 2) specific gravity; 3) spe-
cific volume, cm^3/g; 4) c_p, cal/gram·degree; 5)
Ta^2/c_p, $cm^3/cal·10^{-3}$; 6) K_1, $cm^2/kg·10^{-6}$.

of the compressed air, which have been directed into the space between

the liquefier's tubes. Then the expanded air is diverted through the

heat exchanger 3, cooling the air coming from the compressed-gas engine.

The air in the inter-tube space of the condenser 5 is liquefied

at a pressure of 6-7 atmospheres and then readmitted at the bottom of

the condenser through the regulating valve 6, expanding to 1 atmosphere

in the process. The liquid air is drained from the condenser through

the valve 7.

Liquid oxygen is produced from liquid air by evaporating the nit-

rogen at a temperature of about -190°, after which the liquid oxygen,

which boils at -183°, remains.

The content of oxygen in technical liquid oxygen should be no less

than 99.0% by volume.

Liquid oxygen is used in liquid form as an oxidant for reaction-

thrust fuel. In this state, however, it is physically unstable. As a

result, the storage and transportation of liquid oxygen represent seri-

ous engineering problems.

In its liquid state at atmospheric pressure, oxygen maintains a

constant temperature of -183°, because continuous evaporation of the oxygen is taking place and is related to the absorption of heat. The evaporation of 1 kg of liquid oxygen requires expenditure of 51 kcal of heat. Due to the temperature difference, there is a continuous flow of heat from the surrounding space to the liquid-oxygen container, subject to heat-transfer conditions.

The evaporation time of liquid oxygen is inversely proportional to the heat-transfer surface area and the coefficient of heat transfer from the surrounding air to the liquid oxygen. The latter is basically determined by the thermal-conductivity coefficient of the wall of the container holding the liquid oxygen.

As a result, containers with double walls are used to store liquid oxygen. The space between the walls is heat-insulated with a material having a low thermal conductivity or is evacuated.

It has been established in practice that loose magnesium carbonate powder is an excellent heat-insulation material; this will be evident from comparison of the thermal conductivity coefficients for a number of heat-insulating materials [1].

Magnesium carbonate powder 0.027   kcal/m·hour·degree
Asbestite................. 0.0324   "
Still air................. 0.02   "

Mineral wool and glass wool are also used as heat insulation. The oxygen losses are reduced by 25% when a vacuum jacket is used as heat insulation.

Under laboratory conditions, liquid oxygen is stored in double-walled Dewar flasks with a high vacuum of the order of 0.001 mm Hg between their walls. Small Dewar flasks (1-2 liters) are usually made of glass, while larger flasks (up to 25 liters) are made from metals.

Metal tanks with good heat insulation are used to store and trans-

port large quantities of liquid oxygen. Thus, certain of these have the following characteristics:

	Transportable "tanks"	Stationary "tanks"
Weight of filled "tank," kg....	1100-5000	2500-18,750
Liquid oxygen capacity, liters.	648-2900	1000-12,000
Loss of oxygen per hour, %.....	0.26-0.35	0.12-0.35

Larger "tanks" for storage of liquid oxygen have capacities from 10 to 50 m^3 and may, in some cases, hold as much as 40,000 to 45,000 m^3 [2].

Liquid oxygen tanks with capacities of, for example, 13 or 30 tons are used for long-range hauling of large quantities of liquid oxygen on railroad platform cars. The hourly losses from such tanks come to 0.11-0.12% of capacity [1].

The thickness of the heat-insulation layer in the relatively small "tanks" ranges upward from 250 mm. The tanks are usually cylindrical in shape, since this provides the smallest cooling surface. A pressure of 1.4-1.6 atmospheres is maintained inside the tank, but this increases to 10-15 atmospheres in many stationary tanks.

Since rocket engineering requires large quantities of liquid oxygen, tanks that can accommodate hundreds of tons of this oxidizer are required to provide ready reserves.

A reservoir accommodating 50 m^3 of liquid oxygen was built in 1938 at an experimental air base in Germany. The reservoir consisted of a cylindrical shell having a height and diameter of 8.6 meters, within which an oxygen tank with a diameter of 6 m was placed. The space between the walls of the shell and the inner tank, which was 1.3 meters, was filled with loose magnesium carbonate powder. The reservoir was underground, and this excluded the possibility of heating by sunlight. 140 kg of liquid oxygen, or 0.25%, evaporated daily. If we as-

sume that these losses do not vary as the oxygen reserve changes, about 400 days would be required to evaporate all the oxygen on the basis of these losses.

A plan for a 1,000,000-ton underground liquid-oxygen reservoir has appeared in the literature [3]. The inside diameter of the reservoir's container is 103.5 m and it is 119 meters high. The insulation is 10 meters thick. The quantity of oxygen evaporating daily is 13 tons. Decades would be required for evaporation of all the oxygen from such a reservoir.
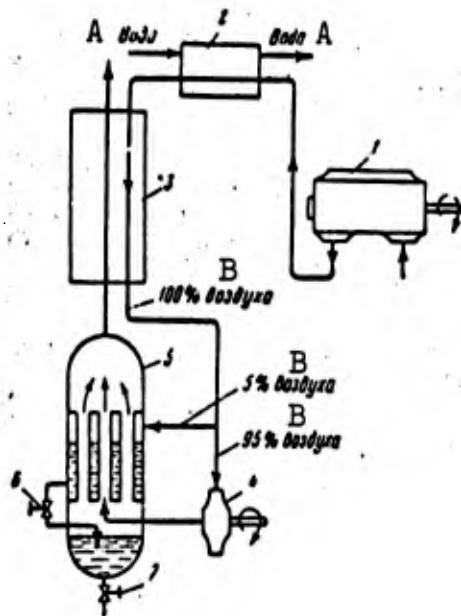
Fig. 231. Diagram of liquid oxygen production by low-pressure refrigerating cycle with compressed-gas engine. 1) Turbocompressor; 2) cooler; 3) heat exchanger; 4) compressed-gas engine; 5) liquefier; 6,7) valves. A) Water; B) air.

As the liquid oxygen evaporates from stationary tanks, the losses are replaced. The gaseous oxygen is compressed to 150 atmospheres and collected in bottles. Gaseous oxygen is also stored under a 150-atmosphere pressure in gas holders with capacities from 750 to 3000 m^3. The gas holders are filled from tank cars carrying liquid oxygen [2].

The storage of liquid oxygen represents a serious problem because of the high chemical activity of oxygen and its extremely low boiling point [3].

Many materials, as, for example, steel and others, become cold-short at low temperatures. Only nonferrous metals and chromium-nickel alloys show good retention of their mechanical properties at low temperatures.

Existing installations and those under construction for the production of oxygen are designed for capacities of 45-225 million m^3/year. Thus, liquid oxygen is one of the cheapest oxidants [1].

According to GOST-4313, oxygen produced from atmospheric air by the deep-freezing method may contain no less than 99% of O_2 for Grade One and no less than 98% of O_2 for Grade Two.

Equipment has been developed for production of liquid oxygen and its aerial transportation. One such unit [4] has a capacity of 8.5 tons of oxygen per day and is designed to service the reaction-thrust engines of long-range rockets with oxygen. It weighs 19.5 tons, but it can be knocked down into several sections for greater convenience in aerial transportation. The assembled installation is 15 meters long, 4 meters wide and 3.3 meters high.

Operation of the installation is automated; it is serviced round the clock by only four workers. A single operator attends it in each shift (8 hours), and one engineer is assigned to the installation for general supervision.

Maximum use is made of aluminum and plastics as structural materials to keep the weight of the installation down.

The installation works on the principle of air-compression and -expansion cycles, with cooling of the air in air condensers and by liquid nitrogen. Liquid oxygen of 99.5% purity issues from a continuous-
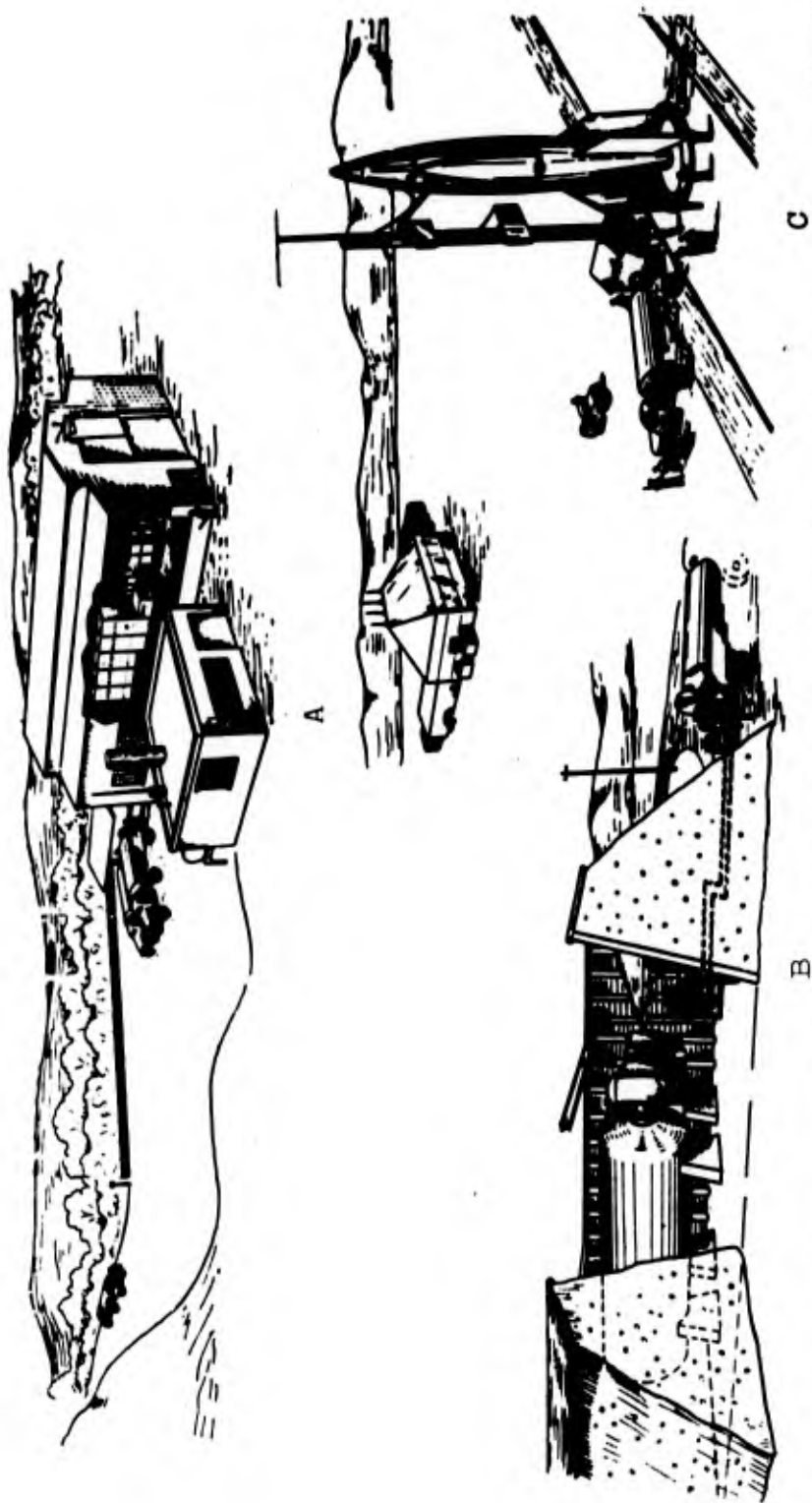
Fig. 232. Liquid-oxygen producing installation that can be dismantled and transported by air (a), storage of liquid oxygen (b), and use of liquid oxygen to service rockets (c).

flow rectification column.

As a rule, liquid oxygen is used at the point of consumption [sic]. However, it can be hauled and stored in special tank cars having a 15,000-liter capacity. It is interesting to note that the reservoirs can be equipped with special automatic helium coolers to condense and return the evaporated oxygen. In the helium cooler, liquid helium (boiling point -269°) circulates through a tube condenser installed in the top of the reservoir containing the liquid oxygen. The gaseous oxygen condenses at its boiling point of -183°. The helium coolers make it possible to store a large quantity of liquid oxygen for a long time and to transport it over long distances without losses.

Figure 232 shows a transportable installation for production of liquid oxygen, its storage, and its use in servicing rockets [4].

2. Ozone

Apart from oxygen, ozone is also considered as an oxidizer for rocket fuels; this application was first suggested by Yu.V. Kondratyuk [5].

Ozone is an allotropic modification of oxygen. Its melting point is 251° [sic] and its boiling point is -111.1°. In the liquid state, ozone has a dark blue color. It is capable of spontaneous decomposition and is distinguished by high brisance as a result of the fact that it is an endothermal compound. The specific weight of liquid ozone at its boiling point is 1.46, while that of oxygen is 1.14. Ozone has limited solubility in liquid oxygen. Thus, for example, the solubility of ozone at the boiling point of oxygen (-183°) is about 25%. Mixtures of oxygen and ozone containing from 25 to 55% of the latter separate into two layers: a heavy dark-violet phase that is richer in ozone (55% O_3) and a lignter light-blue phase richer in oxygen. Solutions containing more than 55% of ozone do not stratify but represent an explosion haz-

ard. At temperatures above -179.5°, ozone mixes with oxygen in all proportions, but elevated pressure is required to keep the solution in its liquid state [2].

The oxygen-ozone diagram of state [6-7] for a pressure of 1 atmosphere is shown in Fig. 233.

Ozone is an unstable substance and is liable to spontaneous decomposition. This reaction is accompanied by the liberation of a large quantity of energy: $2O_3 \rightarrow 3O_2 + 69$ kcal/mole or 720 kcal/kg. The kinetics of this process and the influence of various catalysts on it have been studied. Manganese peroxide, cupric oxide and other substances accelerate the decomposition of ozone. However, perfectly pure ozone is stable at room temperature or, in any event, its decomposition proceeds slowly. Gaseous ozone is capable of explosive decomposition [8].

It was reported in literature data published before 1956 that ozone — both liquid and solid — was a highly explosive substance. Explosions occurred readily on boiling, heating, and shock, as well as when organic materials contaminated the ozone.

According to a report [9] that appeared in 1956, it was established in a study of the properties and stability of liquid ozone that the reason for explosions in liquid ozone was the presence of minute quantities of organic impurities contained in the oxygen from which the ozone had been produced. They can contaminate it from the lubricating oils of the compressor in the production of liquid air and separation of the oxygen. These oils are subject to cracking and oxidation with formation of volatile products that contaminate the oxygen. If the oxygen from which the ozone is produced is first passed through cupric oxide that has been heated to 700°, the organic impurities burn out and the ozone, which is obtained from this oxygen in liquid form,

will possess exceptional stability to shock and vibration and high thermal stability.
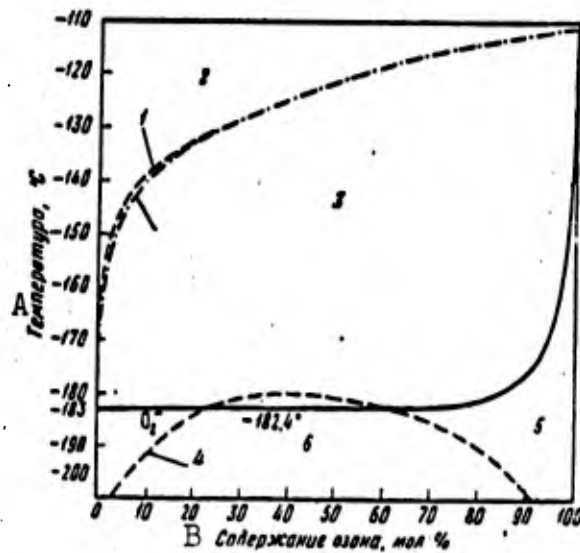
Fig. 233. Diagram of state of ozone-oxygen system for pressure of 1 atm. 1) Ideal solution; 2) vapor; 3) liq-uid and vapor; 4) liquid oxygen; 5) liquid ozone; 6) two liquid phases. A) Temperature, °C; B) ozone content, mole-%.

TABLE 185

Nature of Discharge-Induced Explosion in Mixtures of Ozone with Oxygen [11]

1 Концентрация озона		4 Агрегатное состояние	5 Характер взрыва
2 объемн. %	3 вес %		
11	15,6	6 Газ *	Мягкий 7
14,2	20,0	»	»
25	33,3	»	»
38	47,9	»	Резкий. 8
40	50,0	9 Жидкость **	Сильный взрыв 10
44	54,1	»	Детонация 11

*Initiation of explosion in gaseous phase at voltage of 3000 v and interelectrode distance of 0.8 mm.
**Initiation of explosion in liquid phase with voltage of 15,000 v and interelectrode distance of 0.5 mm.

1) Ozone concentration; 2) % by volume; 3) % by weight; 4) physical state; 5) nature of explosion; 6) gas*; 7) mild; 8) sharp; 9) liquid**; 10) powerful explosion; 11) detonation.

It has been reported [10] that bottles of liquid ozone have been dropped from high altitude and that the impact did not produce explosions. Then liquid ozone was subjected to 60-cycle vibrations for long periods of time, again without explosion as a result.

Ozone produced from oxygen that has not been purified by the above method explodes even on boiling. Ozone explosions begin in the gaseous phase, so that gaseous ozone must be handled with great caution. Tests were carried out to determine the sensitivity of liquid mixtures of ozone with oxygen to pulses produced by high-energy electric discharge. The nature of the explosion in ozone of various concentrations is indicated in Table 185.

TABLE 186

Detonation Velocity in Solutions of Ozone in Oxygen

1 Содержание озона в растворе кислорода, вес. %	2 Скорость детонации, м/сек
47	1840
60	4260
81	6460
96	6840

1) Content of ozone in oxygen solution, % by weight; 2) detonation velocity, m/sec.

The explosive properties of liquid ozone and its solutions in oxygen were studied in the USSR by A.Ya. Apin, S.A. Pshezhetskiy, et al [12]. The properties studied were sensitivity to shock, detonation velocity, and the critical diameter of the tube in which detonation can still propagate.

The researchers established that solutions of ozone in oxygen containing 58% of ozone are close to nitroglycerin as regards their sensitivity to shock.

The detonation rates of the ozone-oxygen solutions were investi-

TABLE 187

Susceptibility of Solutions of Ozone
in Oxygen to Propagation of Detona-
tion from No. 8 Detonator Capsule in
Glass Tubes 20 mm in Diameter

1 Концен-трация озона, вес. %	2 Результаты опытов	3 Примечание
37,4	Детонация не прошла 4	КД № 8 + тетриловая шашка 5
34,4	То же 6	
40,2	Детонация началась и за-тухла 7	
47%	Детонация прошла 8	В растворе CF₄ 9
50%	То же 10	

1) Ozone concentration, % by weight;
2) results of experiments; 3) re-
marks; 4) detonation did not advance;
5) No. 8 capsule detonator + tetryl
cap; 6) same; 7) detonation began
and died out; 8) detonation advanced;
9) in CF_4 solution; 10) same.

gated photographically. The light from detonation of charges of ozone-

oxygen solutions was fixed with a photographic registering device on

high-sensitivity film strips. The detonation rate was computed from

the angle of inclination of the detonation trace on the film. The de-

tonation rate was measured in ozone-oxygen solutions containing 47, 60,

80, and 96% of ozone. The detonation rates in solutions containing 47

to 80% of ozone in oxygen were measured in glass tubes 15-18 mm in di-

ameter. The charge was 250-300 mm long, and was fired by a No. 8 de-

tonator capsule.

The detonation rates of solutions containing 96% ozone were meas-

ured in a 2-mm glass tube 10 cm long. In this case, the detonation was

initiated by a glow wire.

Table 186 shows the results of the detonation-velocity measure-

ments.

No detonation occurred in 37% solutions of ozone in oxygen; Fig.

234 shows the detonation rate of ozone solutions as a function of the ozone concentration in the oxygen. The detonation rate of 100% liquid ozone is about 7000 m/sec, which corresponds to the detonation rate of TNT.
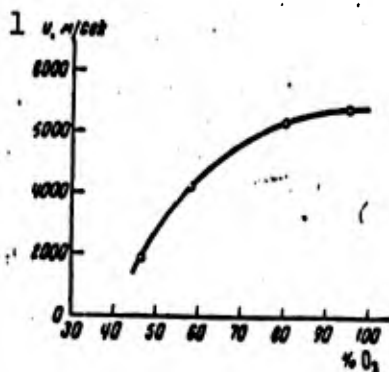
Fig. 234. Detonation rate in ozone-oxygen solutions as function of ozone content. 1) U, m/sec.
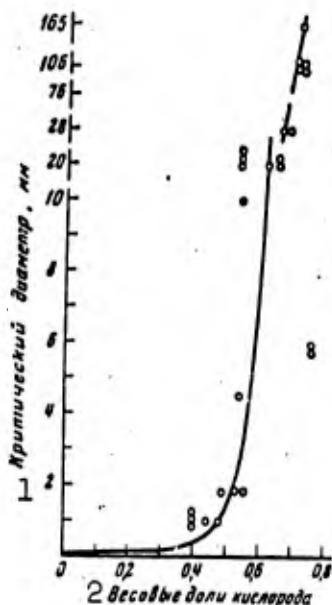
Fig. 235. Critical diameters of ozone-oxygen solutions. 1) Critical diameter, mm; 2) weight fraction of oxygen.

The critical diameter of a liquid-ozone charge, i.e., the minimum charge diameter at which detonation arises, was determined in fine capillaries and glass tubes with diameters of the order of 19-38 mm

TABLE 188

Critical Diameter at which
Propagation of Detonation is
Still Possible in Ozone-Oxygen
Mixtures

1 Содержание озона, вес. %	2 Критический диаметр, мм
32	> 100
37	> 30
47	$< 4,5$
58	$< 0,9$
96	$< 0,15$

1) Ozone content, % by weight;
2) critical diameter, mm.

and wall thicknesses of 0.5 mm (Fig. 235).

In no case was detonation observed when a 33% solution of ozone in oxygen was ignited in glass tubes with diameters up to 38 mm placed inside copper tubes with wall thicknesses from 2.5 to 6 mm. The explosions were initiated by a No. 8 detonator capsule. The results of the experiments are given in Tables 187 and 188.

The data obtained permit approximate evaluation of the critical diameters of ozone-oxygen solutions of various compositions.

Ozone can be produced by many different methods. However, it appears that only two methods can be of technical value: 1) transformation of oxygen into ozone by glow discharge; 2) the thermal method. New methods involving the use of radioactive radiation may also offer interest.

In the former method, oxygen is passed into the space between two glass tubes. The inside of the inner tube and the outside of the outer tube are covered with tinfoil, to which a potential difference of 10,000-50,000 volts is applied, with the result that a silent electric discharge arises between these electrodes and the oxygen is partially converted into ozone. Under such conditions, equilibrium is established

between the oxygen and the ozone. The ozone yield runs as high as 14%.

Ozone can be separated from mixtures with oxygen due to the difference between the boiling points of these two substances. There are reports that if the ozone-producing process is carried out at a temperature near that of liquid air (−190°), with certain modifications to the ozonator design, ozone can be obtained from oxygen with a 99% yield.
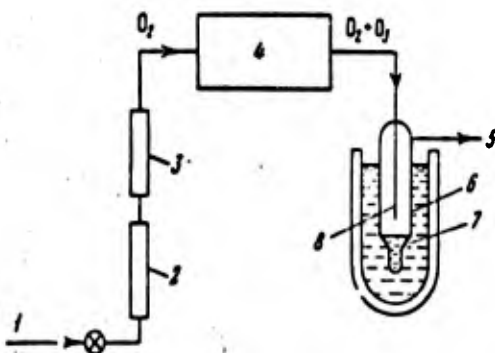
Fig. 236. Diagram of apparatus for producing liquid ozone. 1) Oxygen from bottles; 2) oxygen purifier; 3) feed regulator; 4) ozonator; 5) outlet for gaseous oxygen; 6) coolant, liquid oxygen at −183°; 7) liquid ozone; 8) condenser.

The thermal method of producing ozone consists in partial conversion of oxygen into ozone at high temperatures. On the basis of the equilibrium calculation

$$3O_2 \rightleftarrows 2O_3$$
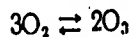
the following quantities of ozone can be obtained in mixtures with oxygen:

| Temperature, °C.............. | 1296 | 2048 | 4500 |
| O_3 yield, % by weight....... | 0.1 | 1.0 | 10.0 |

Decomposition of the ozone can be prevented by rapid cooling of the resulting mixture, so that ozonated oxygen is produced.

It is possible to use liquid oxygen as the starting point for

conversion of oxygen into ozone. For this purpose, a platinum wire is heated in liquid oxygen. On contact with the incandescent solid, the oxygen evaporates and is transformed into ozone, and the ozone dissolves in the liquid and diffuses into the cold oxygen layers. Thus, the liquid oxygen is progressively enriched by ozone up to concentrations of the order of 5%. This method of producing ozone is economically unsuitable because of the large amounts of electric power required and the considerable evaporation of the liquid oxygen, although its simplicity does render it attractive.

It has been proposed that oxygen be converted into ozone by bombardment with fast electrons [11].

Ozone can also be produced by electrolysis of aqueous solutions of sulfuric acid; the result is a gas with a high ozone content [8].

It has been shown [9] that in producing liquid mixtures of ozone with oxygen, it is highly important to guarantee purification of the oxygen entering the mixture, as well as to protect the system from possible contamination. Cleanliness of the apparatus is an extremely important point. Thus, borosilicate-glass apparatus is treated with chromic acid and then washed with distilled water. Before beginning work, the equipment is subjected to treatment with a gas containing from 10 to 50% of ozone mixed with oxygen.

Figure 236 shows a diagram of an apparatus for producing liquid ozone; this was developed in the research center at the Illinois Technological Institute in Chicago [9].

To produce liquid ozone, gaseous oxygen under a pressure of 0.7 kgf/cm^2 is passed through a purifier and enters an ozonator, where from 1 to 6% of ozone is formed. This mixture enters a condenser. The ozone is condensed at a temperature of -112^0 and a partial pressure of 1 kgf/cm^2 and collected in the condenser, while the gaseous oxygen,

- 679 -

the condensation temperature of which is -183°, is diverted from the condenser. The liquid ozone is drained from the condenser as necessary into other containers.
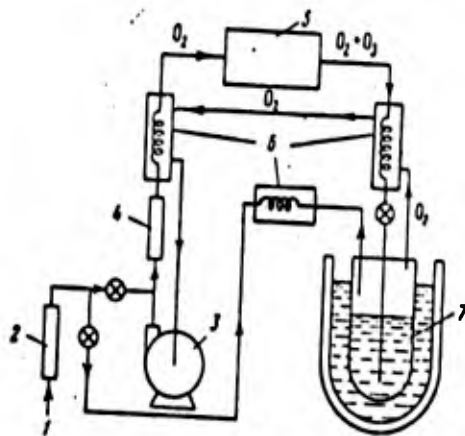
Fig. 237. Diagram of apparatus for producing liquid ozone and mixtures of ozone with oxygen, with oxygen recirculation. 1) Oxygen from bottle; 2) oxygen purifier; 3) recirculation pump; 4) oxygen-feed regulator; 5) ozonator; 6) heat exchangers; 7) solution of ozone in oxygen.
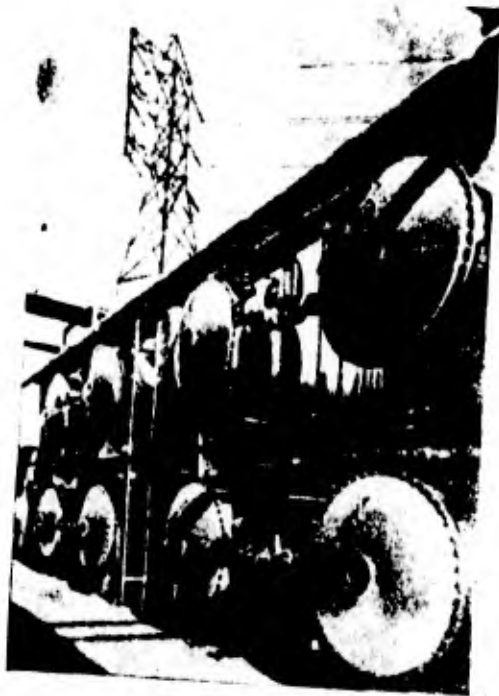
Fig. 238. External appearance of industrial apparatus for producing ozone.
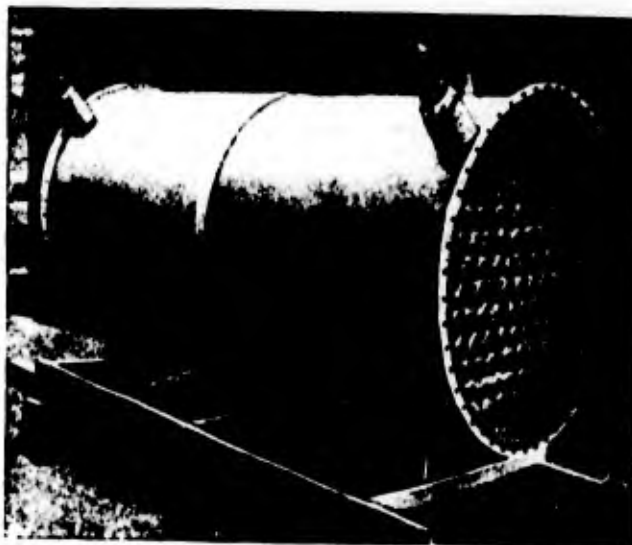
Fig. 239. Industrial reactor for pro-
duction of ozone.

When solutions of ozone in liquid oxygen are produced (Fig. 237),
the gases emerging from the ozonator pass into the condenser through
the liquid-oxygen purifier. Here, the ozone condenses, while the gas-
eous oxygen bubbles through liquid oxygen and is released into the
atmosphere. This process is continued until the ozone concentration
reaches the necessary value; here, it is sometimes necessary to run
additional quantities of purified liquid oxygen into the condenser. To
avoid losses of the purified oxygen passing through the condenser, it
is redirected into the recirculation system.

Recirculation makes it possible to reduce the amount of oxygen
consumed in producing the ozone. Since the evaporating oxygen has a
low temperature, it can be used to cool the gaseous ozone-oxygen mix-
ture arriving from the ozonator, as well as the oxygen entering the
ozonator; special cooling units are set up for this purpose. In this
case, the over-all efficiency of the unit is raised.

According to published reports, the working experience of the Il-
linois Technological Institute research center indicates that when the
necessary precautionary measures' are taken, the experimental apparatus

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is capable of producing highly concentrated gaseous and liquid ozone and can be used without danger of explosion.

However, it should not be forgotten here that ozone is, in itself, an explosive substance, since it has a high heat of decomposition on the same level of those of explosives.

Ozone is in production on an industrial scale at the present time for various technical purposes.

Thus, a report [13] has appeared concerning the performance of an industrial installation for the production of ozone and the engineering problems encountered in using large quantities of ozone in industry, including those of industrial safety; the uses of ozone in technological processes were also touched upon.

Figure 238 shows an industrial installation for producing ozone from oxygen, and Fig. 239 the reactor of this installation.

During storage of solutions of ozone in liquid oxygen, the oxygen evaporates preferentially from solution, with the result that the solution becomes enriched in ozone.

It appears that liquid mixtures of ozone with oxygen are less dangerous beginning at an ozone concentration of about 25%.

To prevent possible ozone-storage-tank explosions, liquid oxygen should be added to these solutions, or helium oxygen condensers should be employed to eliminate oxygen losses.

The question of practical use of ozone as a liquid-rocket oxidant is still open and requires a large volume of scientific research work, although it has been reported in recent years [15] that the USA has solved the problem of using 20-25% solutions of ozone in oxygen and recommended use of such an oxidant for rocket engines.

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Chapter 4

FLUORINE, FLUORINE COMPOUNDS, AND OXYGEN COMPOUNDS OF CHLORINE

1. FLUORINE

During the past ten years, liquid fluorine and certain of its compounds have been subjected to a thorough study with respect to

TABLE 189

Characteristics of Fluorine Oxidizers

1) Окислитель	2) Формула	3) Плотность 18)	4) Молекулярный вес	5) Температура, °C		8) Теплота образования, ккал/мол	9) Вязкость, сантипуазы
				6) плавления	7) кипения		
10) Жидкий фтор	F_2	1,54 при —196°	38,0	—218,0	—188,3	0	0,257 при—190°
11) Перхлорилфторид	$FClO_3$	1,392 при +25°	102,4	—110,0	—46,8	+5,12	
12) Трифторид хлора	ClF_3	1,825 при +20°	92,46	—76	+11,3	+37	4,33 при +20°
13) Пентафторид брома	BrF_5	2,463 при +25°	175	—62,3	+40,76	—	—
14) Трифторид азота	NF_3	1,55 при —129,6°	71,0	—206,63	—128,8	+27,2	—
15) Дифторид кислорода	F_2O	1,63 при —190°	54,0	—233,8	—146,5	—7,6	0,2826 при —145
16) Нитрат фтора	FNO_3	1,61 при —80°	81,0	—181	—80	+1,0	—
17) Тетрафторид гидразина	N_2F_4	—	104	—	—73	—	—

1) Oxidizer; 2) formula; 3) density; 4) molecular weight; 5) temperature, $^{\circ}C$; 6) melting; 7) boiling; 8) heat of formation, kcal/mole; 9) viscosity, centipoises; 10) liquid fluorine; 11) perchlorylfluoride; 12) chlorine trifluoride; 13) bromine pentafluoride; 14) nitrogen trifluoride; 15) oxygen difluoride; 16) fluorine nitrate; 17) tetrafluoride hydrazine; 18) for.

their utilization as oxidizers for rocket propellants.

Among the known fluorine compounds, particular attention is drawn to the following substances (Table 189). Of the enumerated compounds, liquid fluorine, chlorine trifluoride, and bromine pentafluoride are being produced on an industrial scale since the Second World

War. These compounds are being used for the fluorination of uranium in order to separate uranium from waste atomic-reactor fuels and to derive fluorinated hydrocarbons and polymers.

Perchlorylfluoride was first obtained in 1952 and is now being produced by many plants in the USA [1]. Let us examine in detail a number of fluorine oxidizers.

Fluorine and its compounds with oxygen and halogens are powerful oxidizers that far exceed all remaining oxidizers. They are regarded in the literature as possible oxidizers for rocket propellants [1, 2]. Together with hydrocarbons, fluorine yields propellant mixtures exhibiting advantages with respect to energy over oxygen-based propellants. However, the utilization of fluorine as an oxidizer for hydrocarbons is complicated by the high toxicity of fluorine and its low boiling point.
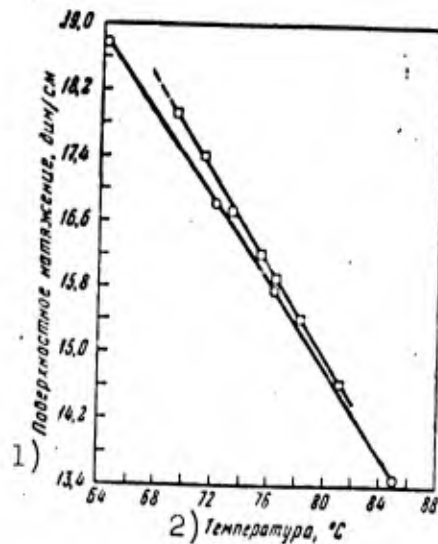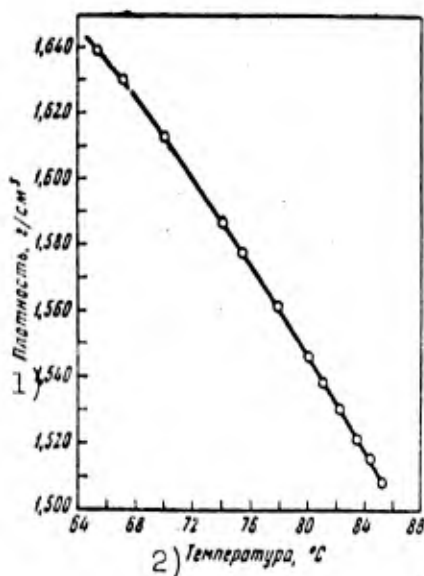
Fig. 240. Change in the density of liquid fluorine as a function of temperature. 1) Density, g/cm^3; 2) temperature, $^{\circ}$C.

Fig. 241. Change in surface tension of liquid fluorine as a function of temperature. 1) Surface tension, dyn/cm; 2) temperature, $^{\circ}$C.

Fluorine — a greenish-green gas and yellow in color in the liquid state — has a boiling point of -188.3° and a melting point of -218°; the latent heat of vaporization is 1.581 kcal/mole [3].

Until recently, concepts with regard to the density of fluorine in the liquid state at the boiling point were based on data derived by Moissan as far back as 1897 [4]. According to Moissan, the density of fluorine is $\rho = 1.14$. In 1937 [5], data on the density of liquid fluorine at the boiling point were published, and these indicated that $\rho_{-187^o} = 1.11$.

Two reports appeared in 1952 [6, 7] on the density of fluorine in the liquid state.

Kel'ner and his co-authors [6] give the density of liquid fluorine for $- 196^o$ as equal to 1.54 ± 0.2.

The Jet Propulsion Laboratory of the California Institute of Technology undertook, on special assignment, a detailed investigation of the density, viscosity, and surface tension of liquid fluorine at temperatures ranging from $- 187$ to $- 207^o$ [7].

The density of liquid fluorine according to this investigation is presented in Table 190.

The graphical change in the density of liquid fluorine as a function of temperature is presented in Fig. 240.

The viscosity of liquid fluorine for various temperatures is presented in Table 191.

The change in the surface tension of liquid fluorine as a function of temperature is presented in Fig. 241.

The viscosity of liquid fluorine, in poises, can also be calculated by the following empirical equation (Table 191):

$$\eta = 2{,}43 \times 10^{-4} \times c^{194/T}$$

According to data from Japanese investigators [5], the vapor pressure of liquid fluorine can be expressed by the following equation:

$$\log p = 9.1975 - (442{\cdot}72/T) - 0.013150{\cdot}T$$

Fluorine occurs in approximately the same quantities in nature

- 686 -

TABLE 190

Density of Liquid Fluorine [7]

1) Температура, °C	2) Плотность	3) Температура, °C	4) Плотность
—207,6	1,639±0,021	—193,0	1,547±0,002
—205,9	1,630±0,002	—192,0	1,539±0,002
—203,0	1,613±0,002	—190,9	1,531±0,002
—199,9	1,587±0,002	—189,6	1,522±0,002
—197,6	1,578±0,002	—188,7	1,516±0,002
—195,2	1,562±0,002	187,8	1,509±0,002

1) Temperature, °C; 2) density; 3) temperature, °C; 4) density.

as does nitrogen or sulfur, and occurs in substantially greater quantities than bromine. Fluorine is extremely toxic, resulting in respiratory tract irritation (a concentration of 0.0008 mg/liter is still toxic). In pure form, gaseous fluorine is also harmful to the skin. As protection against the harmful effects of fluorine, we can

TABLE 191.

Viscosity of Liquid Fluorine as a Function of
Temperature [7]

1) Температура, °C	2) Вязкость, сантипуазы	3) Температура, °C	4) Вязкость, сантипуазы
—203,8	0,414	—194,8	0,2
—199,8	0,349	—192,1	0,275
—197,7	0,328	—190,7	0,257

1) Temperature, °C; 2) viscosity, centipoises;
3) temperature, °C; 4) viscosity, centipoises.

recommend an oxygen gasmask or a mask connected by a tube to a pure-air source.

Fluorine exhibits pronounced chemical activity. For example, it combines with such elements as chlorine and oxygen. Chlorine burns in a fluorine atmosphere. Hydrocarbons burn equally as well in fluorine as they do in oxygen.

In Germany fluorine was stored and transported in steel flasks

under a pressure of 160 atm. Each flask contained 1 kg of fluorine [3]. Fluorine can also be stored in nickel and steel flasks under a pressure of 30 atm [9].

The industrial production of fluorine was undertaken during the Second World War in connection with the needs of the atomic-energy industry. Prior to 1940, fluorine served as a rare chemical reagent.

During the war, in Germany, approximately 50 tons of fluorine were produced each month. The industrial method for the production of fluorine involves the electrolysis of a mixture of potassium fluoride and hydrogen fluoride [8].

The basic source for the derivation of fluorine is fluorite CaF_2. In 1957, 1.7 million tons of this material were obtained throughout the world (without the USSR), of which 0.785 million tons were from the USA.

The known worldwide reserves of fluorspar amount to 66 million tons, having a CaF_2 content in excess of 35%. At the same time, reserves of fluorine with phosphates, on the basis of pure fluorine, amount to 870 million tons, which is equivalent to 1780 million tons of fluorspar. Fluorine-bearing ores are processed into calcium fluoride which, in 1957, was employed in the following areas [1],

```
Metallurgy.......... 241.3 thousand tons (38%)
Chemical industry... 328.7 thousand tons (51%)
Ceramics............  37.3 thousand tons ( 6%)
Other areas.........  35.6 thousand tons ( 5%)
```

Calcium fluoride is used in the chemical industry almost exclusively for the production of hydrogen fluoride of 97-99% purity.

Elementary fluorine is obtained by the electrolysis of a solution of potassium fluoride and hydrogen fluoride; it is purified of HF to a content of 99.9%. The USA produces 1000 tons of fluorine annually. The liquefaction of fluorine is accomplished by cooling it

with liquid nitrogen.

Dry fluorine does not corrode soft steel more actively than liquid oxygen; however, every effort should be made to avoid having the dry fluorine come into contact with organic compounds and water.

Liquefied fluorine is poured into flasks for purposes of transportation; a pressure of up to 27 atm is used for the storage of the fluorine in the flasks. In 1957, in the USA, liquid fluorine cost $13,250 per ton, whereas the cost of liquid oxygen was $110.

Liquid fluorine is apparently being used in rocket engineering at the moment in experimental rocket engines developing thrust of between 5 and 30 tons. Special methods have been developed for this purpose of producing, storing, the transporting liquid fluorine.

Jackets are employed on storage tanks for liquid fluorine, and these jackets are filled with liquid nitrogen having a temperature of -195.5°, whereas fluorine boils at -187.9°. The jacket in turn is vacuum insulated. Liquid fluorine can be stored in a tank of this type for 15 to 25 days, with a daily loss not exceeding 0.75%. Stainless steel, nickel, or aluminum can be used as the material for these tanks. Liquid fluorine can be stored up to 25 days in experimental tanks with a capacity of 2.3 tons. The tank is designed to provide for the storage of liquid fluorine for a period of 24 hours without the liquid-nitrogen jacket. Should it become necessary, liquid fluorine can be transported in special railroad tank cars having a capacity of 25 tons.

Of the organic materials, only teflon is stable in fluorine below 199°. The maximum concentrations of fluorine in air must not exceed 0.0001%.

2. FLUORINE MONOXIDE F_2O AND TETRAFLUOROHYDRAZINE N_2F_4

Among the possible oxidizers, fluorine monoxide deserves special

attention, since it consists of two elements each being a powerful oxidizer.

Vapor pressure (tension), density, and viscosity of F_2O are determined by the following equations [10]:

$$\log p = 7.3892 - (578.64/T)$$

$$\rho = 2.1315 - 0.004695 \cdot T$$

$$\log \eta = (131.5/T) - 1.5768 \text{ (in centipoises, ranging from } - 152.8 \text{ to } -145.8^\circ)$$

The boiling point of a specimen containing 99.8% F_2O is $- 144.8^\circ$ and the melting point is $- 223.8^\circ$ [2]; the critical temperature and pressure is $- 58.0^\circ$ and 48.7 atm, respectively.

Fluorine monoxide is a weak endothermic compound and its heat of formation in the following reaction

$$\tfrac{1}{2}O_2 + F_2 \rightarrow F_2O - 7.6 \text{ kcal/g-mole}$$
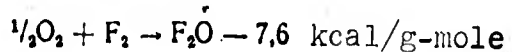
amounts to 130 kcal/kg.

The thermal decomposition of F_2O takes place slowly and the magnitude of its energy of activation within a range of 250 to 270° amounts to 41 kcal/g-mole.

At 300°, 72% F_2O decomposes and forms fluorine and oxygen.

Because of the high energy of decomposition activation, fuorine monoxide can be mixed with hydrogen, methane, and similar substances without producing ignition as is the case when the above-mentioned substances are mixed with fluorine.

Concentrated alkaline solutions quickly decompose fluorine monoxide.

Fluorine monoxide is characterized by pronounced oxidation properties similar to those of ozone.

Fluorine monoxide is produced by passing fluorine through a 27% alkaline solution in the following reaction

$$2F_2 + 2NaOH \rightarrow F_2O + 2NaF + H_2O.$$

The fluorine monoxide yield is 45%. This contains admixtures of oxygen and hydrogen fluoride [10, 11]. The other oxygen fluoride O_2F_2 is unstable and decomposes easily.

In recent years, a new oxidizer for rocket engines has been proposed, i.e., tetrafluorohydrazine N_2F_4 [11a]. This is derived, in addition to nitrogen fluoride, by the fluorination of ammonia:

$$NH_3 + F_2 \rightarrow NHF_2, \ NF_3, \ N_2F_4.$$

A process has been developed in the USA for the derivation [11b] of N_2F_4 from NF_3 and carbon in the boiling layer at 375°C:

$$2NF_3 + \frac{1}{2}C \rightarrow N_2F_4 + \frac{1}{2}CF_4.$$
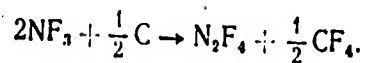
The tetrafluorohydrazine yield is 75%. In addition to the carbon, for the conversion of the nitrogen trifluoride into tetrafluorohydrazine. powders of various metals are recommended, i.e., copper, antimony, etc.

The vapor pressure of tetrafluorohydrazine can be found from the following formula:

$$\log p(mm \ Hg) = - (692/T) + 6.33.$$

The critical temperature for N_2F_4 is + 36° and the critical pressure is −77 atm; the heat of vaporization is 3170 cal/mole.

3. CHLORINE TRIFLUORIDE, BROMINE PENTAFLUORIDE, AND FLUORINE-SUBSTITUTED HYDROCARBONS [3, 8, 12]

Compounds of this type are halogen derivatives of fluorine. These include: ClF, ClF_3, BrF, BrF_3, BrF_5, JF_5, and JF_7.

Chlorine trifluoride is a light-green gas whose boiling point is + 11.3° and whose melting point is − 76.3°.

The density of ClF_3 in the liquid state is equal to 1.85 at the boiling point.

Chlorine trifluoride is an extremely reactive substance. Fiberglas and many organic substances burst into flame on contact. ClF_3 produces an explosion ["a noise like a shot"] on coming into contact

with water.

The boiling point of bromine pentafluoride is $+40.76^{\circ}$, the melting point is -61.23°, and the density is equal to 2.47 at $+20^{\circ}$; at the boiling point the density is equal to -2.41.

The density and vapor pressure of the liquid fluorides ClF_3 and BrF_5 can be calculated according to the following equation:

$$d = A - B \cdot T,$$

where T is the temperature $(^{\circ}K)$; A and B are constants equal to 3.496 and 0.000346 for BrF_5 and equal to 2.729 and 0.00307 for ClF_3. The vapor pressure is determined by the following equation:

$$\log p = D - \varepsilon/T + F/T^2,$$

where D, ε. and F are constants that are equal to 8.0716, 1627.7, and 0 for BrF_3, and equal to 7.42, 1292, and 0 for ClF_3.

The magnitude of the thermal effect of the reaction in which the chlorine trifluoride is formed amounts to:

$$\tfrac{1}{2}Cl_2 + \tfrac{3}{2}F_2 \to ClF_3 + 37,0 \, kcal.$$
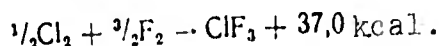
It is assumed that chlorine trifluoride is capable of dimerization according to the following equation:

$$2ClF_3 \to (ClF_3)_2 + 3,3 \, kcal.$$
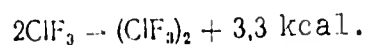
Chlorine trifluoride is obtained through the direct interaction of fluorine with chlorine in a mixture with nitrogen, in a copper or nickel reactor at 280°. A fitting covered with nickel fluoride is placed into the reactor. Chlorine trifluoride is separated from the gas mixture through the cooling of the reaction mixture to -70°.

Chlorine trifluoride can be stored in containers of conventional steel.

Bromine pentafluoride is obtained directly from fluorine and bromine. For this, the fluorine together with the bromine, diluted with nitrogen, are passed through a copper reactor at $200-300^{\circ}$. Bromine

pentafluoride is condensed in the cooling of the reaction mixture to -20°.

Prior to the Second World War, halogen derivatives of fluorine were obtained in small quantities in laboratories and were quite inaccessible.

During the Second World War, as a result of the development of the industrial production of fluorine, the situation changed radically. For example, in Germany, chlorine trifluoride was scheduled for use as an ignitor. In this connection, a plant was built at Falkenhagen and the plant was scheduled for the production of more than 1800 tons of chlorine trifluoride annually.

Chlorine trifluoride and bromine pentafluoride have now become accessible and are being produced industrially. The scale of their industrial production is difficult to evaluate. Approximately in 1950, installations for the production of these materials in the USA were still in the drafting stage. At that time it was assumed that the fluorine halogens will find great industrial application [1].

According to reports in 1956, chlorine trifluoride was regarded as an oxidizer for rocket propellants in the USA [13].

A mixture of $FClO_3$ (40%) and ClF_3 (60%) is of interest as an oxidizer because it exhibits lower vapor pressure than perchlorylfluoride.

In addition to chlorine and bromine fluorides, the USA has undertaken the production of a new oxidizer, i.e., perchlorylfluoride $FClO_3$.

Compounds of fluorine and carbon serve as oxidizers for metals [14], since the splitting of the C-F bond and the formation of the Me-F bond is associated with the liberation of a great quantity of heat:

$$C_nF_{2n} + nMg \rightarrow nMgF_2 + nC + Q.$$
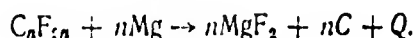
Fluorine-bearing organic compounds are obtained by the action of inorganic compounds of fluorine (CoF_3, MnF_3) or fluorine diluted with nitrogen on hydrocarbons in the presence of catalysts. Under these conditions, all of the hydrogen atoms in the hydrocarbons can be replaced by fluorine, and such compounds are referred to as fluorocarbons. The fluorination of various petroleum fractions results in the production of fluorine-containing liquids that are used as special lubricants. The polymerization of fluoro-olefins such as, for example, tetrafluoroethylene C_2F_4, results in high-molecular fluorine-bearing substances $(C_2F_4)_n$ used as fluorine plastics.

Fluorocarbons and fluorine liquids are extremely stable substances whose boiling point is somewhat lower than that of the initial hydrocarbons (Table 192).

TABLE 192

Properties of Fluorocarbons

1) Исходный углеводород	2) Фторуглерод	3) Т. кип., °C	4) Т. пл., °C	Плотность при 20° 5)
6) Гептан	C_7F_{16}	82	—78	1,783
7) Октан	C_8F_{18}	104	—33	1,790
8) Метилциклогексан	$C_6F_{11}CF_3$	76,3	Низкая 9)	1,799

1) Initial hydrocarbon; 2) fluorocarbon; 3) boiling point, °C; 4) melting point, °C; 5) density at 20°; 6) heptane; 7) octane; 8) methylcyclohexane; 9) low.

The fluorocarbons, obtained from petroleum fractions, and the fluorine plastics are used in industry in working with aggressive media.

The industrial capacity for the production of organic fluorine derivatives in the USA reached 205-245 thousand tons annually in 1957 [16].

TABLE 193

Properties of Oxygen Compounds of Chlorine [15]

1) Соединение	2) Формула	3) Температура, °C		6) Свойства
		4) плавления	5) кипения	
7) Окись хлора	Cl_2O	−20	+ 3,8	Взрывчата 15)
8) Двуокись »	ClO_2	−59	+20	»
9) Шестиокись »	Cl_2O_6	−1	--	Легко взрывает 16)
10) Семиокись »	Cl_2O_7	−91,5	72	То же 17)
11) Хлорноватистая кислота	$HClO$	—	—	Существует только в рас- творах 18)
12) Хлористая кислота	$HClO_2$	—	—	То же
13) Хлорноватая »	$HClO_3$	—	—	» . »
14) Хлорная »	$HClO_4$	−112	—	Не взрывается, но не устой- чива в чистом виде 19)

1) Compound; 2) formula; 3) temperature, °C; 4) melting; 5) boiling; 6) properties; 7) chlorine monoxide; 8) chlorine dioxide; 9) chlorine hexoxide; 10) chlorine heptoxide; 11) hypochlorous acid; 12) chlorous acid; 13) chloric acid; 14) perchloric acid; 15) explosive; 16) explodes easily; 17) the same; 18) exists only in solutions; 19) does not explode, but is not stable in pure form.

4. PERCHLORIC ACID AND OXIDES OF CHLORINE [17]

Oxygen compounds of chlorine are active oxidizers. Anhydrous perchloric acid was suggested as an oxidizer for rocket propellants. Of the oxygen-containing acids of chlorine perchloric acid is the most stable compound. The salts of the oxygen-containing acids of chlorine are quite stable and find practical application as oxidizers in industry and in the fabrication of new rocket powders (grains); however, they are not used in liquid reaction (rocket) propellants. The properties of the oxygen compounds of chlorine are presented in Table 193.

Of the oxygen compounds of chlorine, only perchloric acid is a compound that does not explode in its pure form.

Anhydrous perchloric acid (pure) is a colorless liquid with a specific weight of 1.767 (at 20°), which solidifies at − 112°. It does not distill without decomposition at atmospheric pressure. At a

temperature of about 90°, vigorous decomposition begins. Perchloric acid distills without decomposition only in a vacuum. The boiling point of perchloric acid is $+ 16^{\circ}$ at 18 mm Hg; $+ 30^{\circ}$ at 50 mm; and $+ 50-51^{\circ}$ at 100 mm.

The heat of formation for anhydrous perchloric acid in accordance with the following equation

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 + 2O_2 \rightarrow HClO_4$$
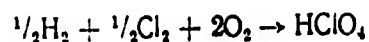
is equal to 19.35 kcal.

The formation of perchloric acid is accompanied by the absorption of heat. This explains its relative stability.

The reaction of the total decomposition of perchloric acid takes place with heat liberation:

$$HClO_4 \rightarrow \tfrac{1}{2}H_2O + \tfrac{1}{2}Cl_2 + 1.75O_2 + 15.7 \text{ kcal.}$$
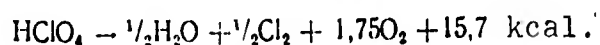
Only 158 kcal are liberated per 1 kg of material, and this is inadequate in order to provide for independent destructive decomposition. Therefore, perchloric acid does not explode under the action of an impact, friction, or a detonator. However, the addition of only 3% of organic substances to the perchloric acid produces an extremely explosive mixture. The organic substance may be dissolved in the perchloric acid without resulting in any chemical interaction, but in the case of heating or impact such a mixture will detonate. Many substances (amines, unsaturated compounds, rubber, paper, fiber, and wood) are hypergolic when placed in contact with perchloric acid. The hypergolic ignition sometimes takes place vigorously, i.e., with an explosion. Pure perchloric acid is not a completely heterogeneous substance. In the equilibrium state, it contains a certain quantity of perchloric anhydride and water, bound to form the hydrate of the perchloric acid. Perchloric anhydride is an unstable substance and decomposes into oxygen and chlorine monoxide, and this serves to ex-

plain the decomposition of the perchloric acid during storage:

$$3HClO_4 \rightleftarrows Cl_2O_7 + H_2O \cdot HClO_4$$
$$Cl_2O_7 \rightarrow 2ClO_3 + 1\tfrac{1}{2}O_3$$
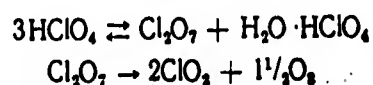
The oxygen is removed from the perchloric acid as it is formed and produces pressure in a closed container. The increase in pressure with time can result in the collapse of the vessel. The chlorine dioxide that is formed has a boiling point of $+ 20^\circ$. It accumulates in the perchloric acid as it is formed, tinting the acid a greenish color at first, then brown, and finally a dark-brown color.

Chlorine dioxide is an extremely unstable substance and the explosions of decomposing perchloric acid can therefore be explained by the apparent accumulation within it of the chlorine dioxide.

The decomposition of perchloric acid is speeded up by the products of the decomposition, i.e., the decomposition is self-catalytic in character. At room temperature, the decomposition of perchloric acid becomes quite pronounced only after several days. At 50°, the total decomposition of perchloric acid ceases after several hours.

Perchloric acid with water forms a series of hydrates and is chemically completely stable in this state. The melting point of a number of hydrates is presented below:

	Melting point, $^\circ$C	Acid concentration, %
$HClO_4$	$- 112$	100
$HClO_4 \cdot H_2O$	$+ 50$	84.4
$HClO_4 \cdot 2H_2O$	$- 17.8$	72

In the distillation of the aqueous solutions of perchloric acid, the boiling point gradually increases to 203.0°, which corresponds to a continuously boiling mixture containing 72.4% $HClO_4$.

Industry generally produces a 30-70% perchloric acid. The density of the 70% $HClO_4$ at 25° is equal to 1.6644.

Only the anhydrous perchloric acid is of interest as an oxidizer. Under laboratory conditions, anhydrous perchloric acid is obtained through the heating of potassium perchlorate with 95% sulfuric acid in accordance with the following reaction:

$$KClO_4 + H_2SO_4 \rightarrow HClO_4 + KHSO_4.$$
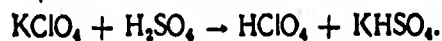
The reaction is carried out with the gradual heating of the reaction mixture from 100 to 200° in a vacuum from 20 to 100 mm Hg. At a pressure of 45-50 mm Hg, perchloric acid boils off at 30-33°. The product of the reaction boils off as it is formed and is condensed in receivers cooled by a mixture of ice and salt. 95% H_2SO_4 should be taken for the reaction, since the 99-100% acid may result in the dehydration of the perchloric acid with the formation of explosive chlorine oxides. Generally 3-4 parts of sulfuric acid are taken for each part by weight of the perchlorate for the reaction, in order to preserve the reaction mass in liquid form upon completion of the reaction. The perchloric-acid yield is 80-90% of the theoretical. The purest perchloric acid is obtained when 94-95% sulfuric acid and a vacuum of 10-20 mm Hg are used. The resultant perchloric acid contains about 1% of impurities (H_2SO_4, HCl, and H_2O). With a sulfuric acid of higher concentration, a product colored greenish, yellow, or brown, by the chlorine oxides, may be produced.

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PHYSICOCHEMICAL PROPERTIES OF ROCKET
COMBUSTIBLES AND OXIDIZERS [1-4]

Physicochemical Properties of Combustibles

Triethylamine $(C_2H_5)_3N$

Molecular weight..................... 101.19

Melting point........................ $-114.8^{\circ}C$

Boiling point........................ $89.5^{\circ}C$

Density

°c	g/cm³
−40,0	0,784
+20,0	0,729
+25,0	0,723

Critical temperature................. $262.0^{\circ}C$

Critical pressure.................... 30.0 atm

Saturation Vapor Pressure

°c	mm Hg	°c	mm Hg	°c	mm Hg
9,8	30,0	39,0	125,5	80,0	580,0
15,7	40,0	48,7	190,7	89,5	700,0
16,7	43,5	70,0	400,0	143,0	2870,0
30,9	86,5				

Heat of combustion at $20.0^{\circ}C$ (liquid)   1036.8 kcal/g-mole

Viscosity

°c	centipoises	°c	centipoises
−70,0	1,67	77,0	0,51
−40,0	1,18	110,0	0,44

Refractive index n_D^{20}................ 1.40032

Diethylenetriamine $H_2NC_2H_4NHC_2H_4NH_2$

Molecular weight................................. 103.17

Boiling point.................................... $206.7^{\circ}C$

Density at 20.0°C.................................... 0.956 g/cm^3

Coefficient of thermal expansion at 20.0°C.......... 0.00088 cm^3/deg

Saturation vapor pressure at 120.0°C................ 622.0 mm Hg

Viscosity at 120.0°C................................ 71.4 centipoises

Ethylenediamine $H_2NC_2H_4NH_2$

Molecular weight.................................... 60.10

Melting point....................................... 8.5°C

Boiling point....................................... 116.1°C

Density at 20.0°C................................... 0.8994 g/cm^3

Saturation vapor pressure at 21.5°C................. 10.0 mm Hg

Heat of fusion at 0.0°C............................. 77.0 cal/g

Heat of evaporation................................. 167.0 cal/g

Heat of combustion.................................. 452.6 kcal/mole

Viscosity at 25.0°C................................. 1.54 centipoises

Refractive index $n_D^{26.0}$........................ 1.4540

Unsymmetric Dimethylhydrazine $(CH_3)_2NNH_2$

Molecular weight.................................... 60.078

Melting point....................................... −52.0°C

Boiling point....................................... 63.0°C

Density at 22.0°C................................... 0.7914 g/cm^3

Critical temperature................................ 249.0°C

Critical pressure................................... 60.0 atm

Coefficient of thermal expansion at 15.6°C.......... 0.00133 cm^3/deg

Surface tension at 77.0°C........................... 28.0 dynes/cm

Heat of fusion at −52.0°C........................... 10.0 cal/g

Heat of evaporation at 25.0°C....................... 139.3 cal/g

Heat capacity (solid)

°c	cal/mole·deg	°c	cal/mole·deg
−260,2	0,66	−183,2	11,50
−253,2	1,82	−143,2	14,99
−243,2	3,74	− 93,2	19,12
−213,2	8,32	− 57,5	22,48

Heat capacity (liquid)

°c	cal/mole·deg	°c	cal/mole·deg
−57,2	36,25	− 8,2	38,07
−43,2	36,86	+ 1,8	38,40
−28,2	37,44	+11,8	38,78
−18,2	37,76	+25,0	39,20

Heat of formation.. −187.3 cal/g

Heat of combustion at 30.0°C.......................... 7866.7 cal/g

Entropy at 25.0°C (liquid)............................ 47.86 cal/mole·deg

   "   "   "   (gas)................................ 72.8 cal/mole·deg

Viscosity at 15.6°C................................... 0.586 centipoise

Refractive index $n_D^{25.0}$......................... 1.4056

Hydrogen H_2*

(Normal hydrogen, which is a mixture
of ortho- and para-hydrogen)

Molecular weight...................... 2.01418

Melting point......................... −259.1°C

Boiling point......................... −252.7°C

Density

°c	g/cm³	°c	g/cm³	°c	g/cm³
−258,2	0,0755	−250,2	0,0670	−244,2	0,0560
−256,2	0,0738	−248,2	0,0640	−242,2	0,0503
−254,2	0,0718	−246,2	0,0604	−240,2	0,0356
−252,2	0,0695				

Critical temperature.................. −239.9°C

Critical pressure..................... 12.80 atm

Critical density...................... 0.031 g/cm³

Coefficient of thermal expansion (solid)

°c	cm³/deg
−269,0	0,0024
−262,2	0,0051

Coefficient of thermal expansion (liquid)

°C	atm	cm^3/deg	°C	atm	cm^3/deg
−253,2	2,0	0,0156	−240,0	50,0	0,0196
−253,2	10,0	0,0137	−253,2	100,0	0,0078
−242,2	10,0	0,0911	−240,0	100,0	0,0114
−253,2	50,0	0,0098			

Compressibility coefficient (liquid)

°C	atm	cm^3/deg	°C	atm	cm^3/deg
−253,2	2,0	0,00186	−240,0	50,0	0,00297
−253,2	10,0	0,00159	−253,2	100,0	0,00076
−242,2	10,0	0,02168	−240,0	100,0	0,00140
−253,2	50,0	0,00103			

Saturation vapor pressure (liquid)

°C	mm Hg	°C	mm Hg
−259,2	54,0	−253,2	675,7
−259,1	57,0	−251,2	1189,0
−257,2	153,0	−250,2	1529,6
−255,2	345,9	−249,6	1753,3

Saturation vapor pressure of 100% ortho-hydrogen

°C	mm Hg	°C	mm Hg
−259,1	55,1	−251,2	1170,4
−257,2	149,1	−250,2	1508,4
−255,2	337,8	−249,6	1730,8
−253,2	662,6		

Surface tension of hydrogen (liquid)

°C	dynes/cm	°C	dynes/cm
−257,2	3,00	−251,2	1,88
−255,2	2,60	−249,2	1,50
−253,2	2,25		

Heat of fusion at −259.2°C and 54.0 mm Hg........... 28.0 cal/mole

Heat of fusion of hydrogen vapor at 259.4°C [sic]
and 52.8 mm Hg................................ 28.0 cal/mole

Heat of evaporation (liquid)

°C	cal/mole
−258,2	219,00
−253,2	216,58

Heat of evaporation of hydrogen vapor (liquid)

°C	cal/liter	°C	cal/liter
−255,2	7998,093	−249,2	6622,077
−253,2	7654,089	−247,2	6002,870
−251,2	7155,283	−245,2	5332,062

Heat capacity (liquid)

°c	cal/mole·deg	°c	cal/mole·deg
−259,2	3,31	−255,2	4,04
−258,2	3,46	−254,2	4,27
−257,2	3,63	−253,2	4,50
−256,2	3,83		

Heat capacity of hydrogen vapor (liquid)

°c	cal/mole·deg	°c	cal/mole·deg
−254,9	4,18	−248,2	6,03
−252,3	4,71	−245,6	7,85
−250,5	5,33	−241,2	14,56

Heat of formation (gaseous)

	°c	cal/mole		°c	cal/mole
H	−273,18	51 620,0	H⁺	25,0	367 088,0
H	25,0	52 089,0	H_2	−273,18	0,0
H⁺	−273,18	365 138,0	H_2	25,0	0,0

Heat of combustion at 25°C......................... 28,669.6 cal/g

Entropy (liquid)

°c	atm	cal/mole·deg	°c	atm	cal/mole·deg
−253,2	2,0	0,013	−253,2	50,0	0,396
−253,2	10,0	0,095	−243,2	50,0	1,000
−243,2	10,0	0,125	−253,2	100,0	0,663
−253,2	30,0	0,261	−243,2	100,0	1,481
−243,2	30,0	0,692	−243,2	150,0	1,792

Enthalpy

°c	atm	cal/mole	°c	atm	cal/mole
−253,2	2,0	0,488	−253,2	100,0	50,283
−253,2	10,0	4,262	−243,2	100,0	23,452
−253,2	30,0	14,131	−243,2	150,0	46,222
−253,2	50,0	24,327			

Viscosity (liquid)

°c	centipoise	°c	centipoise
−258,1	$229,3 \cdot 10^{-6}$	−254,4	$160,0 \cdot 10^{-6}$
−256,9	$204,6 \cdot 10^{-6}$	−253,9	$151,9 \cdot 10^{-6}$
−255,4	$177,2 \cdot 10^{-6}$	−252,5	$136,2 \cdot 10^{-6}$

Dielectric constant of hydrogen (liquid)

°c	ε	°c	ε
−259,2	1,2501	−254,6	1,2343
−256,8	1,2421	−253,6	1,2301
−255,7	1,2387	−252,8	1,2278

Anhydrous Hydrazine N_2H_4

Molecular weight...................... 32.05

Melting point........................ +1.4°C

Boiling point

atm	°c
1,0	113,0
1,96	134,5

Density at −4.4°C (solid)............. 1.146 g/cm^3

Density (liquid)

°c	g/cm^3
0,0	1,0258
0,2	1,0256
20,0	1,0085

Density of saturated vapor

°c	mm Hg	g/cm^3	°c	mm Hg	g/cm^3
90,0	265,0	0,000365	110,0	287,0	0,000365
95,0	273,0	0,000365	120,0	294,0	0,000365
100,0	277,0	0,000365	131,0	747,0	0.000952

Critical temperature................. 380.0°C

Critical pressure.................... 145.0 atm

Critical volume...................... 138.6 cm^3/mole

Saturation vapor pressure

°c	mm Hg	°c	mm Hg	°c	mm Hg
0,0	2,69	35,0	25,67	55,0	72,85
15,0	7,65	40,0	33,82	60,0	92,43
20,0	10,55	45,0	44,08	65,0	116,30
25,0	14,38	50,0	56,91	70,0	145,12
30,0	19,29				

Surface tension

°c	dynes/cm
20,0	74,76
40,0	69,76

Heat of fusion at 25.0°C............................. 94.5 cal/g

Heat of evaporation at 25.0°C....................... 10,700.0 cal/mole

Heat capacity (solid)

°c	cal/mole·deg	c°	cal/mole·deg	°c	cal/mole·deg
−261,2	0,07	−193,2	5,96	−93,2	11,36
−253,2	0,35	−173,2	7,37	−73,2	12,19
−233,2	2,13	−133,2	9,57	−33,2	13,86
−213,2	4,23				

Heat capacity (liquid)

°c	cal/mole·deg	°c	cal/mole·deg	°c	cal/mole·deg
1,7	23,29	25,0	23,62	47,0	23,96
7,0	23,37	27,0	23,65	57,0	24,14
17,0	23,51	37,0	23,80	67,0	24,34

Heat of formation at 25°C (liquid)... −376.30 cal/g

Heat of combustion at 25°C (liquid).. 4640.0 cal/g

Entropy at 25°C (liquid)............. 0.9052 cal/g·deg

Enthalpy at 25°C (liquid)........... 56.6 cal/g

Viscosity (liquid)

°c	centipoises	°c	centipoises	°c	centipoises
0,0	1,314	3,0	1,251	15,0	1,044
1,0	1,293	5,0	1,207	20,0	0,974
2,0	1,272	10,0	1,118	25,0	0,905

Refractive index

°c	n_D
35,0	1,4644
25,0	1,4687
20,0	1,4708

n-Propyl Nitrate $CH_3CH_2CH_2ONO_2$

Molecular weight..................... 105.09

Melting point....................... −101.1°C

Boiling point....................... 110.5°C

Density (liquid)

°c	g/cm^3	°c	g/cm^3	°c	g/cm^3
−50,0	1,1419	10,0	1,0696	140,0	0,8935
−30,0	1,1182	30,0	1,0445	190,0	0,8127
−20,0	1,1062	60,0	1,0087	240,0	0,7154
−10,0	1,0941	90,0	0,9654	290,0	0,5664

Critical temperature............................. 307.0°C

Critical pressure.................................... 40.0 atm

Critical density.................................... 0.356 g/cm^3

Coefficient of thermal expansion at 20.0°C......... 0.000955 cm^3/deg

Saturation vapor pressure

°C	atm	°C	atm	°C	atm
—50,0	0,00004	10,0	0,01370	140,0	2,20000
—30,0	0,00070	30,0	0,04230	190,0	6,59000
—20,0	0,00170	60,0	0,16900	240,0	15,80000
—10,0	0,00350	90,0	0,51700	290,0	32,20000

Surface tension

°C	dynes/cm	°C	dynes/cm
17,8	27,45	40,9	24,45
22,3	27,02	58,4	22,53

Heat of evaporation

°C	cal/mole	°C	cal/mole
20,0	9590,0	160,0	7400,0
40,0	9280,0	210,0	6300,0
70,0	8270,0	260,0	4600,0

Heat capacity at 25.0°C.............. 0.419 cal/g·deg

Viscosity

°C	centipoises	°C	centipoises
—78,5	6,1	30,0	0,58
—58,0	3,0	40,0	0,50
—30,0	1,4	60,0	0,38
0,0	0,99		

Refractive index n_D^{20}................ 1.3979

Theoretical characterization of combustion of n-propyl nitrate

Combustion chamber pressure, atm	Temperature in combustion chamber, °K	Specific impulse, sec
20.4	—	167
20.4	1252	166
20.4	1276	169
54.4	1325	186
68.0	—	190

Isopropyl Nitrate $(CH_3)_2CHONO_2$

Molecular weight..................... 105.09

Boiling point....................... 102.0°C

Density at 18.9°C.................... 1.036 g/cm^3

Physicochemical Properties of Oxidizers [1, 3, 4]

Tetranitromethane C(NO$_2$)$_4$

Molecular weight....................... 196.043

Melting point......................... +14.2

Boiling point......................... 126.0°C

Density (liquid)

°C	g/cm^3
13,0	1,650
25,0	1,630

Saturation vapor pressure

°C	mm Hg	°C	mm Hg
0,0	1,9	80,0	164,0
20,0	8,4	100,0	339,0
40,0	75,8	125,0	743,0
60,0	68,0		

Heat of fusion at 14.2°C............. 2250.6 cal/mole

Heat of evaporation at 125.7°C....... 9200 cal/mole

Heat capacity (solid)

°C	cal/mole·deg	°C	cal/mole·deg	°C	cal/mole·deg
−215,1	17,14	−154,7	28,25	−63,3	50,99
−196,1	21,06	−131,2	31,48	5,5	63,36
−182,3	23,55	− 99,3	43,41	10,0	88,38

Heat capacity (liquid)

°C	cal/mole·deg
19,1	57,36
25,8	58,19

Heat of combustion.................... 89.6 kcal/mole

Viscosity at 20.0°C................... 1.76 centipoises

Refractive index

°C	n_D
20,0	1,43840
25,0	1,43580

Perchloryl Fluoride ClO$_3$F

Molecular weight...................... 102.457

Melting point......................... −110.0°C

Boiling point........................ −46.8°C

Density (liquid)

°c	g/cm³	°c	g/cm³	°c	g/cm³
−140,0	1,981	−70,0	1,770	0,0	1.518
−130,0	1,952	−60,0	1,737	10,0	1.478
−120,0	1,923	−50,0	1,700	20,0	1,434
−110,0	1,894	−40,0	1,669	30,0	1,389
−100,0	1,864	−30,0	1,634	40,0	1,339
− 90,0	1,833	−20,0	1,597	50,0	1,287
− 80,0	1,802	−10,0	1,559		

Critical temperature............................... +95.21°C

Critical pressure................................... 53.00 atm

Critical density.................................... 0.637 g/cm³

Coefficient of thermal expansion for 0.0-10.0°C..... $24.0 \cdot 10^{-4}$ cm³/deg

Compressibility coefficient at 80.0°C............... $3.25 \cdot 10^{-3}$ atm^{-1}

Saturation vapor pressure

°c	atm	°c	atm	°c	atm
−120,0	0,004	−17,78	3,241	54,44	24,161
−90,0	0,074	− 6,67	4,808	71,11	34,081
−70,0	0,290	10,00	7,923	82,22	42,102
−34,44	1,715	26,67	12,512	93,93	51,349
−28,99	2,141	37,78	16,512		

Surface tension

°c	dynes/cm
−75,2	24,05
−65,9	22,31
−55,7	21,25

Heat of evaporation

°c	cal/mole
−46,8	4600,0
−25,0	3500,0

Heat capacity (liquid)

°c	cal/mole·deg	°c	cal/mole·deg
−50,0	0,225	20,0	1,261
−40,0	0,229	40,0	0,277
−20,0	0,238	60,0	0,307
0,0	0,249	80,0	0,395

Heat capacity at constant pressure (gaseous)

°c	cal/mole ·deg	°c	cal/mole ·deg	°c	cal/mole ·deg
−173,16	8,461	526,8	22,968	2726,8	25,593
− 73,2	12,074	726,8	23,882	3726,8	25,696
126,8	18,153	1726,8	25,301	4726,8	25,746
326,8	21,321				

Heat of formation at 25.0°C.......... +5.1200 cal/mole

Entropy at 25.0°C (gaseous).......... 66.51 cal/mole·deg

Viscosity (liquid)

°c	centipoise	°c	centipoise	°c	centipoise
−80,0	0,620	−30,0	0,298	20,0	0,184
−70,0	0,521	−20,0	0,267	30,0	0,170
−60,0	0,444	−10,0	0,240	40,0	0,158
−50,0	0,384	0,0	0,219	50,0	0,148
−40,0	0,337	10,0	0,200	60,0	0,139

Chlorine Trifluoride ClF_3

Molecular weight..................... 92.46

Melting point........................ −82.6°C

Boiling point........................ 11.3°C

Density (liquid)

°c	g/cm^3
−4,07	1,8970
1,70	1,8806
9,64	1,8566
12,68	1,8476
20,92	1,8218
26,90	1,8031
38,71	1,7654
45,63	1,7431

Density of saturated vapor

°c	g/cm^3
0,0	0,0027
12,0	0,0040
40,0	0,0105

Critical temperature................. 174.0°C

Critical pressure.................... 57.0 atm

Saturation vapor pressure

°c	mm Hg	°c	mm Hg
−46,97	20,06	12,24	775,88
2,37	503,67	21,02	1107,60

Boiling point........................ $-46.8^{\circ}C$

Density (liquid)

°c	g/cm³	°c	g/cm³	°c	g/cm³
−140,0	1,981	−70,0	1,770	0,0	1,518
−130,0	1,952	−60,0	1,737	10,0	1,478
−120,0	1,923	−50,0	1,700	20,0	1,434
−110,0	1,894	−40,0	1,669	30,0	1,389
−100,0	1,864	−30,0	1,634	40,0	1,339
− 90,0	1,833	−20,0	1,597	50,0	1,287
− 80,0	1,802	−10,0	1,559		

Critical temperature................................ $+95.21^{\circ}C$

Critical pressure.................................. 53.00 atm

Critical density.................................. 0.637 g/cm³

Coefficient of thermal expansion for $0.0-10.0^{\circ}C$..... $24.0 \cdot 10^{-4}$ cm³/deg

Compressibility coefficient at $80.0^{\circ}C$............... $3.25 \cdot 10^{-3}$ atm^{-1}

Saturation vapor pressure

°c	atm	°c	atm	°c	atm
−120,0	0,004	−17,78	3,241	54,44	24,161
−90,0	0,074	− 6,67	4,808	71,11	34,081
−70,0	0,290	10,00	7,923	82,22	42,102
−34,44	1,715	26,67	12,512	93,93	51,349
−28,99	2,141	37,78	16,512		

Surface tension

°c	dynes/cm
−75,2	24,05
−65,9	22,31
−55,7	21,25

Heat of evaporation

°c	cal/mole
−46,8	4600,0
−25,0	3500,0

Heat capacity (liquid)

°c	cal/mole·deg	°c	cal/mole·deg
−50,0	0,225	20,0	1,261
−40,0	0,229	40,0	0,277
−20,0	0,238	60,0	0,307
0,0	0,249	80,0	0,395

Heat capacity at constant pressure (gaseous)

°c	cal/mole·deg	°c	cal/mole·deg	°c	cal/mole·deg
−173,16	8,461	526,8	22,968	2726,8	25,593
− 73,2	12,074	726,8	23,882	3726,8	25,696
126,8	18,153	1726,8	25,301	4726,8	25,746
326,8	21,321				

Heat of formation at 25.0°C.......... +5.1200 cal/mole

Entropy at 25.0°C (gaseous).......... 66.51 cal/mole·deg

Viscosity (liquid)

°c	centipoise	°c	centipoise	°c	centipoise
−80,0	0,620	−30,0	0,298	20,0	0,184
−70,0	0,521	−20,0	0,267	30,0	0,170
−60,0	0,444	−10,0	0,240	40,0	0,158
−50,0	0,384	0,0	0,219	50,0	0,148
−40,0	0,337	10,0	0,200	60,0	0,139

Chlorine Trifluoride ClF_3

Molecular weight...................... 92.46

Melting point........................ −82.6°C

Boiling point........................ 11.3°C

Density (liquid)

°c	g/cm^3
−4,07	1,8970
1,70	1,8806
9,64	1,8566
12,68	1,8476
20,92	1,8218
26,90	1,8031
38,71	1,7654
45,63	1,7431

Density of saturated vapor

°c	g/cm^3
0,0	0,0027
12,0	0,0040
40,0	0,0105

Critical temperature................. 174.0°C

Critical pressure.................... 57.0 atm

Saturation vapor pressure

°c	mm Hg	°c	mm Hg
−46,97	20,06	12,24	775,88
2,37	503,67	21,02	1107,60

Surface tension (liquid)

°c	dynes/cm	°c	dynes/cm	°c	dynes/cm
0,0	26,6	14,6	24,3	38,0	20,3
4,0	26,0	20,6	23,1	42,0	20,0
9,0	25,1	25,5	22,7	49,9	18,7

Heat of fusion at -76.32°C............ 1819.3 cal/mole

Heat of evaporation at 11.75°C....... 6580.0 cal/mole

Heat capacity (solid)

°c	cal/mole· ·deg	°c	cal/mole· ·deg
−259,12	1,03	−170,32	12,43
−250,42	2,67	−146,62	14,16
−232,49	8,42	−112,55	16,59
−216,86	10,96	− 94,54	17,88

Heat capacity (liquid)

°c	cal/mole· ·deg	°c	cal/mole· ·deg
−76,32	26,68	−24,55	27,38
−68,33	26,78	− 3,30	27,84
−56,63	26,94	5,09	28,02
−46,21	27,05		

Heat capacity at constant pressure (gas)

°c	cal/mole· ·deg	°c	cal/mole· ·deg
− 23,16	14,48	626,89	19,20
26,89	15,58	926,89	19,48
326,89	18,45	1226,89	19,63

Free energy (gaseous)

°c	cal/mole	°c	cal/mole
− 23,16	54,81	626,89	71,84
26,89	56,80	926,89	76,54
326,89	65,71	1226,89	80,34

Free energy of formation

°c	cal/mole	°c	cal/mole
−23,16	30 970,0	626,89	−11 050,0
26,89	29 410,0	1226,89	− 6650,0
326,89	20 130,0		

Entropy at 11.75°C (liquid)......... 43.66 cal/g·deg

Entropy (gaseous)

°c	cal/mole· ·deg	°c	cal/mole· ·deg
−23,16	2647,5	626,89	14 274,0
26,89	3399,0	926,89	20 088,0
326,89	8610,0	1226,89	25 950,0

Viscosity (liquid)

°c	centipoise	°c	centipoise
17,3	0,448	32,6	0,380
17,7	0,447	36,3	0,365
19,4	0,438	39,8	0,352
26,0	0,407	48,0	0,323

Fluorine F_2

Molecular weight...................... 38.00

Melting point........................ −218.0°C

Boiling point........................ −188.3°C

Density (liquid)

°c	g/cm^3	°c	g/cm^3
−207,4	1,638	−191,4	1,532
−201,4	1,594	−188,8	1,514
−198,2	1,578	−188,1	1,505
−194,6	1,550		

Critical temperature................. −129.2°C

Critical pressure.................... 55.0 atm

Saturation vapor pressure

°c	mm Hg	°c	mm Hg	°c	mm Hg
−219,6	1,67	−203,6	84,30	−190,1	604,12
−215,6	6,94	−200,6	139,67	−188,1	763,08
−212,7	17,89	−196,0	280,40	−185,6	1002,72
−206,6	48,12	−193,1	412,75	−183,8	1219,89

Surface tension

°c	dynes/cm	°c	dynes/cm
−216,1	14,61	−207,9	13,17
−213,2	14,16	−202,2	12,20
−211,7	13,85	−191,7	10,41

Heat of fusion at −219.6°C........... 390.0 cal/mole

Heat of evaporation at −185.95°C
(liquid)........................ 1560.0 cal/mole

Heat capacity (solid)

°c	cal/mole·deg	°c	cal/mole·deg
−258,2	1,167	−237,8	5,561
−253,1	2,240	−230,1	7,120
−247,7	3,440	225,2	7,741
−251,2	4,795	—	

Heat capacity (liquid)

°c	cal/mole·deg	°c	cal/mole·deg
−219,6	13,700	−203,2	13,558
−213,2	13,680	−193,2	13,793
−208,2	13,607	−188,1	13,948

Heat capacity at constant pressure (gaseous)

°c	cal/mole·deg	°c	cal/mole·deg	°c	cal/mole·deg
−187,9	6,950	126,8	7,848	1726,8	8,881
−153,2	6,960	226,8	8,187	2726,8	9,258
− 73,2	7,110	426,8	5,535	3726,8	9,388
− 33,2	7,270	626,8	8,722	4726,8	9,510
26,8	7,445	1226,8	8,989		

Heat capacity at constant volume at 25.0°C (gaseous)   5.535 cal/mole·deg

Entropy (liquid)

°c	cal/mole·deg	°c	cal/mole·deg
−219,6	14,586	−203,2	18,245
−218,2	14,955	−193,2	20,067
−213,2	16,146	−188,2	20,907

Enthalpy (gaseous)

°c	cal/mole	°c	cal/mole	°c	cal/mole
−183,2	626,0	−113,2	1123,0	−33,2	1817,0
−173,2	695,0	− 93,2	1280,0	−13,2	2024,0
−153,2	834,0	− 73,2	1440,0	6,8	2255,0
−133,2	977,0				

Viscosity at −188.2°C (liquid)....... 0.24 centipoise

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