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USE OF AUTOMOTIVE GASOLINES

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ABSTRACT: The scientific essentials of the use of automotive gasolines in internal combustion spark-ignition engines are presented. The principal correlations in the development of modern engine requirements on the quality of fuels used and methods of upgrading the main operating properties of automotive gasolines are discussed. The monograph contains a generalization of work done by the author and other domestic and foreign workers in recent years. It is intended for engineering technical personnel engaged in the production of automotive gasolines, their storage and transporting, and also in the operation and development of automotive engines. The volume may prove useful to students at higher educational centers in the appropriate specializations.

NOTICE

The contents of this publication have been translated as presented in the original text. No attempt has been made to verify the accuracy of any statement contained herein. This translation is published with a minimum of copy editing and graphics preparation in order to expedite the dissemination of information.

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INTRODUCTION

In recent years questions of the quality and use of automotive gasolines have taken on wholly new importance and have risen to the plane of the most important problems on whose solution depends technical advances and economic growth. At the present time requirements on the quality of automotive gasolines are very high and new gasolines with improved operating characteristics have to be developed for new engines.

The development of new gasolines and improvement of existing ones must be carried out with allowance for the interests of the automotive and petroleum refining industries, and also organizations operating vehicles. On how successfully a gasoline is selected depends the longevity of an engine, its reliability, and its operating economy. On the other hand, selection of a gasoline determines the direction in which advances are made in petroleum refining. Overstated demands on gasoline quality lead to unjustified outlays in mastering new processes of producing these fuels and, therefore, lead to an increase in their price and higher costs in operating engines. Understated requirements lower the service time of engines, and their longevity and operating reliability, and complicate automotive servicing.

During the past 40 years, the foundations of the science of the properties and uses of fuels and oils in engines have been laid; lately this science has been referred to as "chemmotology" [khimmotologiya]. Chemmotology was born as a science at the frontier between several related disciplines and is now being developed by representatives of the machinebuilding and petroleum refining industries and organizations operating equipment. Chemmotology of automotive gasolines is a part of the science, while this book is the first attempt to summarize materials on the properties and uses of automotive gasolines in engines.

All requirements that are imposed on fuels for internal combustion engines with spark ignition can be conventionally divided into four groups.

1. Fuel properties must ensure the production of a homogeneous air-fuel mixture of requisite composition at any automotive operating temperature

conditions. This requirement governs such fuel qualities as volatility (fractional composition and pressure of saturated vapor), elemental composition, surface tension, density, viscosity, rate of diffusion of vapor in air, heat of vaporization, heat capacity, gum content, and so on.

A fuel that has optimal values for these indicators ensures operating economy of an automotive engine, good starting qualities at different temperatures, rapid warmup and high response [acceleration], minimum wear in the piston-cylinder group, icing-free operation of the carburetor, minimum content of deposits in the intake system, and so on.

2. Fuel qualities must ensure normal combustion of the air-fuel mixture at all engine operating regimes with maximum power-output and operating economy indicators. This requirement governs such fuel qualities as heat of combustion, group hydrocarbon composition, content of nonhydrocarbon impurities, knocking tendency, and glowing ignition, and so on.

A fuel having optimal values for these indicators ensures longevity of an automotive engine, its operating economy, minimum smoking and toxicity of spent gases, and so on.

3. No difficulties must develop during the transportation, storage, and supplying of fuel through the supply system to the engine in any climatic conditions. This requirement governs such fuel qualities as storage stability, content of corrosive compounds, freezing and cloud points, variation in viscosity with temperature, content of mechanical impurities, tendency to suffer losses from vaporization, solubility of water and air, and so on.

Fuel with optimal values of these indicators ensures the operating reliability of an automotive engine at different ambient air temperatures.

4. The fuel must not be expensive, as nontoxic as possible, and its production must be possible with crude oil resources.

Many individual organic compounds and their mixtures meet the listed requirements to some degree. However, they are best satisfied by mixtures of hydrocarbons boiling within the limits from 30-40 to 200-210° C and which are referred to as gasolines.

Automotive gasolines are prepared by processing crude oils, natural gases, coals, peat, and oil shale. In most countries petroleum is the main feed in the production of automotive gasolines. At the present time, even in countries where petroleum reserves are low, automotive gasolines are produced from crude oil imported from other countries.

In USSR nearly all the commercial automotive gasolines is produced from crude oil. Only in the Estonian SSR and adjoining areas are automotive gasolines produced by processing local oil shale successfully used.

Among other products of petroleum refining, automotive gasolines are produced and consumed in the greatest amount: one-third of the crude extracted worldwide is refined into automotive gasoline.

The plans for expansion of the automotive industry provide for simultaneous production growth of both carburetor as well as diesel automotive engines. Carburetor engines will be installed in passenger cars and in some types of trucks, therefore in the immediate future the importance of automotive gasolines will continue.

SYMBOLS

ε = engine compression ratio
n = crankshaft rmp
d = diameter of engine cylinder, mm
φ = crank angle, °
θ = ignition advance angle, ° CA [°CA. = crank angle before top dead center BTDC
L_0 = amount of air theoretically required for combustion, kg/kg
α = coefficient of air excess
ρ_4^t = relative density at temperature t, ° C
ν = kinematic viscosity, cst [centistokes]
r = heat of vaporization, kcal/kg
P_{sat} = saturated vapor pressure, mm Hg
$t_{i.b}$, $t_{e.b}$, t_n, $t_{v.l}$, and t_c = temperatures, respectively, of beginning and end of fuel distillation, distillation of n percent fuel, of air at which vapor locking occurs, and of air at which a cold engine can be started, ° C
ON = octane number
ΔON = change in octane number
RM and MM = Research and Motor methods of determining octane number, respectively
ON_f = requirements of engine for fuel octane number
ONRM and ONMM = octane number, respectively, based on the Research and Motor methods
F = fuel sensitivity, equal to ONIM — ONMM
AON = actual octane number
ONR = octane number in road conditions
OND = distribution octane number
$ONRM_m$ = ONRM, where m is the amount of fractions distilled from the gasoline, percent
$ONRM_{100}$ = octane number of fractions boiling up to 100° C

CHAPTER ONE
COMPOSITION OF GASOLINES

The operating qualities of automotive gasolines are determined by chemical composition. Gasolines consist of hydrocarbons and nonhydrocarbon impurities -- sulfur, nitrogen, and oxygen compounds.

Hydrocarbon Composition

Present-day commercial automotive gasolines are prepared by blending gasolines (components) obtained by direct distillation, cracking, reforming, alkylation, and other processes of refining petroleum and hydrocarbon gases.

Straight-run gasolines. The content of given hydrocarbons in straight-run gasolines depends entirely on their presence in the initial crude, since virtually all chemical changes in the crude occurs during the direct distillation process [1-3]. Gasoline fractions are the most closely studied part of crude [4-41].

The composition of straight-run gasolines includes hydrocarbons in only three classes: paraffinic, naphthenic, and aromatic.

Gasoline fractions of the well-defined paraffinic crudes of Bashkiria, Tataria, and other regions contain more than 50 percent paraffinic hydrocarbons. Gasoline fractions of Baku crudes of the naphthenic type contain more than 50 percent naphthenic hydrocarbons. Molecules of hydrocarbons containing 5-12 carbon atoms are present in gasolines. However, gaseous hydrocarbons even with a smaller number of carbon atoms can be present in small amounts in gasolines.

General correlations on the content in gasoline fractions of hydrocarbons with different structures obtained for large numbers of crudes examined reduce to the following.

Gasolines with a low content of aromatic hydrocarbons as a rule contain many naphthenic hydrocarbons, among which six-membered hydrocarbons predominate. Paraffinic hydrocarbons of these gasolines have branched structures.

When there is a high content of aromatic hydrocarbons in gasolines, many paraffinic hydrocarbons predominantly of normal structure are present, and among the naphthenic hydrocarbons whose content here is limited five-membered compounds predominate.

Normal-structure hydrocarbons predominate in gasoline fractions of methane-base crudes, among the paraffinic hydrocarbons. These hydrocarbons often amount to 50 percent and more of the content of all isomers. The distribution of isomers among paraffinic hydrocarbons has several points of distinction. The predominance of isomers with a single alkyl group is noticeable in all fractions; the content of di-substituted hydrocarbons is somewhat less, and there is very little three and four-substituted hydrocarbons. The vast majority of isomers have only methyl groups in their side chains. Hydrocarbons with methyl and longer side chains are found in a very small amount among C_7 - C_{10} hydrocarbons.

In monosubstituted paraffinic hydrocarbons, the methyl groups are most often located at positions 2 and 3. Hydrocarbons with this structure are contained in greatest amount, while the content of other isomers is minor. There is particularly a large amount of isomers with methyl group in position 2.

There is a considerably narrower diversity among naphthenic hydrocarbons. Straight-run gasolines contain methyl-substituted cyclopentane and cyclohexane in greatest amount. The content of ethyl-substituted cyclopentane and cyclohexanes is lower than of their methyl-substituted counterparts, but as a rule is higher than propyl- and isopropyl-substituted cyclopentanes and cyclohexanes.

Usually gasoline fractions of various crudes contain more cyclohexane hydrocarbons than cyclopentane [6].

Gasoline fractions of crudes contain also bicyclic naphthenic hydrocarbons. Their content with respect to the total of naphthenic hydrocarbons represents less than 1 percent in the 122-150° C fraction, an average of 5 percent in the 150-175° C fraction, and 15 percent in the 175-200° C fraction [28].

The ratio between cyclohexane hydrocarbons of various structures usually persists also for aromatic hydrocarbons in the gasoline fraction of the same crude.

All straight-run gasolines contain less benzene than toluene, while the total xylene content exceeds the toluene content. The meta isomer predominates among the xylenes.

Straight-run gasoline fractions are found to contain all the isomers of aromatic hydrocarbons with nine carbon atoms; and there is roughly twice as much trimethylbenzene than other C_9 hydrocarbons [35].

Our knowledge about the individual hydrocarbon composition of gasolines depends most directly on the methods of analysis employed. With advances and improvement in the methods of studying composition, more and more new hydrocarbons are found in gasoline fractions. Thus, in one of the recent studies [26] on the individual hydrocarbon composition of gasoline fractions (i.b. [initial boiling point] -- 111° C) of five Soviet crudes using liquid-gas chromatography, the content of seven hydrocarbons out of 38 whose presence is possible in this fraction was quantitatively determined. It is obvious that gasoline fractions of various crudes can contain virtually all possible isomers of hydrocarbons in various classes, but their amount depends mainly on the conditions of crude oil formation, the degree of its transformation, depth of the deposit, and so on.

However, it must be noted that in spite of the obvious diversity, the hydrocarbons found are distributed in gasolines prepared from various crudes quite unevenly. Below, as an example, are listed hydrocarbons which are contained in greatest amount in three gasolines prepared from various crudes:

	Content, percent
Surakhan' sampled crude	
Methylcyclohexane	20.05
Cyclohexane	7.37
1, 3-Dimethylcyclohexane	5.68
1, 2-Dimethylcyclopentane	5.49
Methylcyclopentane	4.59
1, 2, 4-Trimethylcyclopentane	3.45
2-Methylhexane	3.16
1, 1-Dimethylcyclohexane	2.99
Ethylcyclohexane	2.23
1, 2, 3-Trimethylcyclopentane	2.05
Total	57.06
Tuymazy crude	
n-Heptane	9.74
n-Hexane	8.43
n-Octane	7.12
n-Pentane	6.32
n-Butane	4.69

2-Methylheptane	4.69
Methylcyclohexane	3.74
2-Methylbutane	3.57
2-Methylhexane	3.43
2-Methylpentane	3.06
Total	54.79

Kokchagyl crude

Methylcyclohexane	13.06
1, 3-Dimethylcyclohexane	6.19
Cyclohexane	4.64
1, 2, 4-Trimethylcyclopentane	4.10
2-Methylbutane	3.55
Methylcyclopentane	3.51
1, 1, 3-Trimethylcyclopentane	3.39
1, 2, 3-Trimethylcyclopentane	2.52
1, 2-Dimethylcyclopentane	2.39
1, 2-Dimethylcyclohexane	2.27
Total	45.62

From these data we see that about half of the component composition of gasolines is represented by ten hydrocarbons, and four hydrocarbons contained in greatest quantity represent one-third of gasolines.

Predominating hydrocarbons in gasolines from various crudes differ widely from each other and obviously the properties of specifically these hydrocarbons determine the properties of gasolines as a whole.

Cracking gasolines. Gasolines obtained by cracking crude oil, in contrast to straight-run gasolines, contain hydrocarbons of the following four classes: paraffinic, naphthenic, aromatic, and olefinic. The appearance of olefinic hydrocarbons is associated with the fact that in the cracking of crude oil large molecules of hydrocarbons with a large number of carbon atoms are cleaved into smaller. Some of the molecules formed constitute olefinic hydrocarbons. In addition to cleaving hydrocarbons, during cracking naphthenic hydrocarbons undergo dehydrogenation, resulting in the cracking gasolines containing more aromatic and less naphthenic hydrocarbons compared with straight-run gasolines (Table 1).

The increased content of aromatic hydrocarbons in cracking gasolines is also accounted for the fact that the crude for cracking consists of heavy crude oil fractions that are richer in aromatic hydrocarbons;

Table 1. Group Hydrocarbon Composition (in Percent by Volume) of Straight-run and Thermal Cracking Gasolines From the Same Crudes

Продукт 1	Непредельные 2	Ароматические 3	Нафтеновые 4	Парафиновые 5
Бензин прямой перегонки (Баку) 6	0	3,7	52,7	43,6
Крекинг-бензин (Баку) 7	25,6	11,7	9,4	53,3
Бензин прямой перегонки (Грозный) 8	0	3,0	32,3	64,7
Крекинг-бензин (Грозный) 9	27,6	16,4	6,2	49,8

Key:
1 -- Product
2 -- Unsaturated
3 -- Aromatic
4 -- Naphthenic
5 -- Paraffinic
6 -- Straight-run gasoline (Baku)
7 -- Cracking gasoline (Baku)
8 -- Straight-run gasoline (Groznyy)
9 -- Cracking gasoline (Groznyy)
[Commas indicate decimal points.]

furthermore, in cracking conditions lower aromatic hydrocarbons are extremely resistant and are converted into gaseous products to a lesser extent than in naphthenic and paraffinic hydrocarbons.

While the composition of straight-run gasolines as a whole is determined by the composition of the starting crude, the composition of cracking gasolines depends to a large extent on the conditions in which the cracking process is carried out. In thermal cracking conditions, as the thermal regime of cracking is intensified, the content of unsaturated hydrocarbons in the resulting gasolines rises. In catalytic cracking, the content of unsaturated hydrocarbons in gasolines depends on the fractional composition of the crude, the temperature conditions of the process, the properties of the catalyst, and so on (cf. below).

A study made of the group hydrocarbon composition of thermal and two-stage catalytic cracking gasolines from Groznyy crude [42] show (Table 2) that these gasolines differ widely in content of unsaturated and aromatic hydrocarbons. Thermal cracking gasoline contains 45 percent unsaturated, and 11 percent aromatic hydrocarbons, while catalytic cracking gasoline, in contrast, has considerably more aromatic (33 percent) and less unsaturated (11 percent) hydrocarbons. Catalytic cracking gasoline has an especially appreciable rise in the concentration of aromatic hydrocarbons in the higher-boiling fractions.

Table 2. Content of Hydrocarbons (in Percent) in Cracking Gasolines From Groznyy Crude [42]

1 Пределы выкипания фракции, °C	2 Выход, % от фракции 60—200 °C	Непредельные 3				9 Ароматические	10 Гексаметиленовые	11 Пентаметиленовые	12 Парафиновые
		циклические 4			8 ациклические				
		5 шестичленные	6 пятичленные	7 ароматические					
Бензин термического крекинга 13									
60—95	18	4,6	11,8	—	34,1	4,7	5,1	5,9	33,8
95—122	20	7,2	16,7	1,2	24,5	9,3	10,4	6,4	24,3
122—150	23	8,3	13,0	2,3	21,3	13,3	8,7	7,4	25,7
150—200	39	8,1	9,0	1,8	21,4	13,9	9,8	6,4	30,6
Бензин каталитического крекинга 14									
60—95	30	0,4	6,5	—	9,1	5,1	4,7	18,3	55,9
95—122	17	—	7,0	2,5	3,3	16,5	16,8	15,0	38,9
122—150	18	—	5,3	—	6,3	42,6	12,7	7,7	25,4
150—200	35	2,0	1,2	0,7	3,1	60,3	6,8	4,4	21,5

Key:
1 -- Fraction boiling limits
2 -- Yield, percent of 60-200° C fraction
3 -- Unsaturated
4 -- cyclic
5 -- six-membered
6 -- five-membered
7 -- aromatic
8 -- acyclic
9 -- Aromatic
10 -- Hexamethylene
11 -- Pentamethylene
12 -- Paraffinic
13 -- Thermal cracking gasoline
14 -- Catalytic cracking gasoline
[Commas indicate decimal points.]

The fractional distribution of unsaturated hydrocarbons (Table 2) in catalytic and thermal cracking gasoline differs. Thermal cracking gasoline contains about 7 percent unsaturated hydrocarbons with a six-membered carbon atom ring, while this group of unsaturated hydrocarbons is virtually absent in catalytic cracking gasolines. The content of unsaturated hydrocarbon with a five-membered ring is nearly three times as much in thermal cracking gasoline as in catalytic cracking gasoline.

A study of the individual hydrocarbon composition of cracking gasoline involves considerable methodological difficulties, therefore there are very few works in this direction [8, 27, 41-45].

In light fractions of thermal cracking gasoline [43], about 50 percent of the composition is accounted for by n-pentane, 2-methylbutane, and 2-methylbutene-2, with a strong predominance of n-pentane. In light fractions of catalytic cracking gasoline from naphthenic crude, about 54 percent is represented by 2-methylbutane and 2-methylbutene-2; the content of n-pentane is only about 3 percent [43]. Light fractions of thermal cracking gasoline contain 1.5-2.5 times more n-paraffins than isoparaffins, while a considerable predominance of isoparaffins over n-paraffins has been noted in catalytic cracking gasoline (by a factor of 10-15). Among the olefinic hydrocarbons, the ratio of n-olefin concentration to isoolefin concentration is about the same for both thermal and catalytic cracking gasolines. In all cases, the isoforms predominate over the normal (by about twofold).

Among the individual paraffin hydrocarbons in thermal cracking gasolines [43], the predominance of normal (~ 74 percent of the total paraffin) and 2-methyl-substituted (~20 percent) is representative. n-Heptane (~22 percent), n-hexane (~ 15 percent), n-octane, and n-nonane (in amounts of more than 12 percent each) are present in highest concentration. The paraffin hydrocarbons with a quaternary carbon atom account for only 1.2 percent of the total paraffin hydrocarbons. Tetra-substituted alkanes have been found only as traces [43].

Among the naphthenic hydrocarbons, about 60 percent are cyclohexane, 30 percent cyclopentane, and 3 percent cyclobutane, which have not been detected in straight-run gasolines. The aromatic hydrocarbons are represented by only 6 percent in thermal cracking gasoline [43]; of the aromatic hydrocarbons, more than half is represented by toluene (1.72 percent) and m-xylene (1.43 percent).

Similar data have been obtained in investigation of the individual hydrocarbon composition of gasolines from various kinds of cracking of American crude gas oil [41]. The total of three normal-structure C_5, C_6, and C_7 paraffinic hydrocarbons in thermal cracking gasoline amounts to 65.4 percent, in straight-run gasolines -- 36.9 percent, in catalytic cracking gasolines -- 11.3 percent, and in hydrocracking gasoline -- only about 3 percent.

In catalytic cracking gasoline, the content of aromatic hydrocarbons is about equal to the total content of naphthenic and paraffinic hydrocarbons, while in thermal cracking gasoline naphthenic and paraffinic hydrocarbons are present in three times the amounts as aromatic.

The content of aromatic hydrocarbons in catalytic cracking gasolines depends only on the conditions of the process and the nature of the crude. Thus, when high-paraffinic kerosene-gas oil feed undergoes catalytic cracking in field conditions, a gasoline is produced containing 25 percent aromatic hydrocarbons, but if the conditions are drastic -- gasoline

Table 3. Composition of Unsaturated Hydrocarbons (in Percent by Weight) in Thermal Cracking Gasoline Fractions [4]

1 Пределы выкипания фракций, °C	2 Всего непредельных	3 Диеновых	4 н-Олефиновых	5 С двойной связью в боковой цепи		8 [illegible]
				6 ароматических	7 [illegible]	
60—95	45,0	2,4	35,1	0,0	[illegible]	[illegible]
95—122	37,0	2,3	26,1	0,0	8,6	[illegible]
122—150	34,8	1,9	20,9	3,3	8,5	0,2
150—175	31,7	1,5	6,8	4,7	18,7	0,0
175—200	26,5	1,1	3,3	7,2	11,9	[illegible]
9 Выше 200	20,5	1,0	4,9	7,2	[illegible]	6,9

Key:
1 -- Fraction boiling limits
2 -- Of total unsaturated
3 -- Dienic
4 -- n-Olefinic
5 -- With double bond in side chain
6 -- aromatic
7 -- cyclo-olefinic and naphthenic
8 -- Unsaturated, not subject to hydrogenation
9 -- Upwards of 200

prepared from the same feed has 58 percent aromatic hydrocarbons [44]. With increasing severity of the conditions, the use of benzene, toluene, ethylbenzene, p-xylene, and certain other aromatic hydrocarbons are considerably greater. When heavy crude undergoes catalytic cracking, the content in gasoline of unsaturated hydrocarbons, including aromatic hydrocarbons with double bonds in side chains, is significantly increased [45].

Data on the composition and structure of unsaturated hydrocarbons in gasolines are of special interest, since it is precisely these hydrocarbons that determine some of the most important operating qualities of gasolines.

For a long time it was believed that unsaturated hydrocarbons in cracking gasolines are generally aliphatic in structure and are classified as mono-olefins [46]. In most recent studies, when selective catalytic hydrogenation was used [47, 4], it was possible to show that unsaturated cyclic-structure hydrocarbons are present. Thus, in the selective catalytic hydrogenation of thermal cracking gasoline containing 36 percent by weight of unsaturated hydrocarbons, it was found that 33 percent of the unsaturated hydrocarbons are converted to paraffins, 37 percent -- to naphthenes, and 30 percent -- to alkylaromatic hydrocarbons [4]. Therefore, the initial gasoline contained olefins, cyclo-olefins, and aromatic hydrocarbons with double bonds in side chains.

When a study was made of unsaturated hydrocarbons in various fractions of thermal cracking gasoline (Table 3), it was found that olefins predominated among the unsaturated hydrocarbons in the light fractions (60-150° C), cyclo-olefins -- in fractions falling within the limits 150-200° C, while aromatic hydrocarbons with double bonds in side chains appear in fractions above 122° C and represent 30-35 percent by weight of all unsaturated hydrocarbons contained in the higher fractions.

Reforming gasolines. The main purpose of reforming lies in improving the quality (knock resistance) of gasoline fractions. As a result of reforming, the knock resistance of gasoline increases by several tens of octane numbers [48-50].

In industrial conditions, gasoline reforming is carried out without a catalyst (thermal reforming) and in the presence of various catalysts (catalytic reforming). Thermal reforming of gasoline fractions has not gained wide acceptance owing to the limited possibilities of this process in increasing knock resistance and owing to the considerable decrease in the yield of gasoline fractions. Gasolines with octane numbers of the order of 70 can be obtained by thermal reforming.

The process of thermal reforming is used at several refineries in the Soviet Union to raise the octane number of straight-run gasolines in order to economize on ethyl fluid [51-56]. This measure was viewed as a temporary expedient until adequate capacities in catalytic reforming were built [49].

Thermal cracking gasolines contain large amounts of unsaturated hydrocarbons, including those with two double bonds. These gasolines are subject to oxidation by air oxygen and have low chemical stability. The group hydrocarbon composition of thermal cracking gasolines is shown in Fig. 1. The top fractions contain about 45 percent aliphatic olefins, while the heavy fractions contain cyclo-olefins in the amount of 10-15 percent [7].

Catalytic reforming, which has become one of the leading processes in the petroleum industry, has gained the greatest acceptance. In addition to improving the quality of gasolines, catalytic reforming is used in producing aromatic hydrocarbons, which are the most valuable feed for organic synthesis.

At the present time, most catalytic reforming facilities operate with a platinum catalyst; the process has been called platforming [57-63]. In platforming conditions, there is a significant aromatization of the gasoline fractions, mainly through dehydrogenation of the naphthenes. Not only the six-membered naphthenes, but also the five-membered naphthenes with side chains undergo dehydrogenation. In this case at first the five-membered naphthenes are isomerized into six-membered, followed by dehydrogenation to the aromatic hydrocarbons (dehydro-isomerization). Paraffinic hydrocarbons in platforming conditions undergo dehydrocyclization, forming

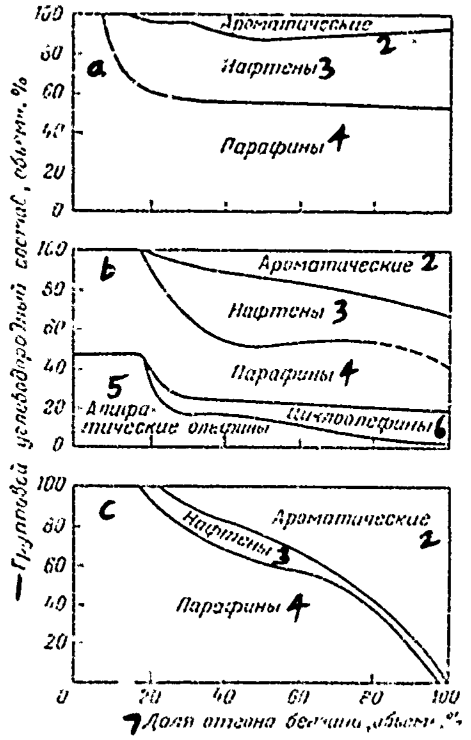

Fig. 1. Content of various hydrocarbons in straight-run gasoline (a), thermal reforming gasoline (b), and platforming gasoline (c) from the same crude [7]

Key: 1 -- Group hydrocarbon composition, percent by volume
2 -- Aromatic
3 -- Naphthenes
4 -- Paraffins
5 -- Aliphatic olefins
6 -- Cyclo-olefins
7 -- Fraction of gasoline distillate

aromatic hydrocarbons (from C_6 and higher) and isomerization (C_4 - C_5). High-molecular paraffin hydrocarbons can in platforming conditions be subject to hydrocracking, forming low-molecular hydrocarbons.

As the result of reforming in the presence of a platinum catalyst, the density of gasoline rises; the beginning-boiling point decreases somewhat and the end-boiling point rises; the content of aromatic hydrocarbons increases sharply; and knock resistance is greater (Table 4).

Table 4. Change in Properties of Gasoline Fractions From Various Crudes Resulting From Catalytic Reforming [58]

Показатель 1	Нефть 2				
	туймазинская (девонская) 3	ромашкинская 4	ухтинская 5	долинская 6	румынская 7
Сырье 8					
ρ_4^{20} 9	0,745	0,745	0,760	0,766	0,761
Фракционный состав, °C					
$t_{н.к.}$ 10	106	105	111	108	107
t_{10}	113	110	120	119	110
t_{50}	131	138	144	136	126
t_{90}	160	162	183	169	169
$t_{к.к.}$ 11	171	184	—	187	177
Углеводородный состав, вес. % 12					
ароматические 13	12,0	11,0	10,6	22,1	15,9
нафтеновые 14	24,0	26,7	42,9	32,3	44,0
парафиновые 15	64,0	62,3	16,5	45,6	40,1
ОЧММ 16	39,0	37,0	—	49,7	47,0
Бензин 17					
ρ_4^{20} 9	0,766	0,768	0,783	0,790	0,7[illegible]8
Фракционный состав, °C					
$t_{н.к.}$ 10	58	38	55	53	65
t_{10}	81	71	98	91	94
t_{50}	119	123	136	126	124
t_{90}	163	165	180	168	16[illegible]
$t_{к.к.}$ 11	191	202	227	201	19[illegible]
Углеводородный состав, вес. % 12					
ароматические 13	52,7	54,8	59,0	61,1	60,1
нафтеновые + парафиновые 18	45,9	44,0	40,0	37,9	38,[illegible]
непредельные 19	1,4	1,2	1,0	1,0	1,0
ОЧММ 16	80	80	80	80	80

Key:
- 1 -- Indicator
- 2 -- Crude
- 3 -- Tuymazy (Devonian)
- 4 -- Romashkin
- 5 -- Ukhta
- 6 -- Dolin
- 7 -- Romanian
- 8 -- Crude
- 9 -- Fractional composition
- 10 -- $t_{i.b}$
- 11 -- $t_{e.b}$
- 12 -- Hydrocarbon composition, percent by weight
- 13 -- aromatic
- 14 -- naphthenic
- 15 -- paraffinic
- 16 -- ONMM
- 17 -- Gasoline
- 18 -- naphthenic + paraffinic
- 19 -- unsaturated

Table 5. Composition and Properties of Catalytic Reforming Gasolines [63]

Показатель 1	Обычный режим риформинга 2	Жесткий режим риформинга 3	
		промышленная установка 4	опытная установка 5
Октановое число без присадок 6			
ММ 7	77	85	86
ИМ 8	81	95	98
Фракционный состав, °C 9			
$t_{н. к.}$ 10	38	42	47
t_{10}	58	67	91
t_{50}	95	121	130
t_{90}	154	161	170
$t_{к. к.}$ 11	180	193	203
Групповой углеводородный состав, вес. % 12			
ароматических 13	31,6	61,7	68,2
нафтеновых 14	3,1	1,9	1,9
парафиновых 15	64,5	36,4	29,9
непредельных 16	0,8	Нет 17	Нет 17

Key:
1 -- Indicator
2 -- Usual reforming conditions
3 -- Drastic reforming conditions
4 -- industrial facility
5 -- pilot plant
6 -- Octane number without additives
7 -- Motor Method
8 -- Research Method
9 -- Fractional composition
10 -- $t_{i.b}$
11 -- $t_{e.b}$
12 -- Group hydrocarbon composition, percent by weight
13 -- aromatic
14 -- naphthenic
15 -- paraffinic
16 -- unsaturated
17 -- None

The content of aromatic hydrocarbons in platforming gasoline depends to a large extent on the conditions of the process (Table 5). In ordinary conditions, the content of aromatic hydrocarbons in the resulting gasoline is 35-40 percent, and in drastic conditions -- 60-70 percent.

Ordinary-regime reforming gasolines contain considerable amounts of normal paraffin hydrocarbons (22.9-23.4 percent), and their content reaches a value of 9-13 percent even in drastic-regime reforming gasolines. Among the normal paraffin hydrocarbons there is a predominance of butenes, pentanes, and hexanes, which obviously is associated with the use of feedstock of leaned fractional composition.

Among the paraffin hydrocarbons, iso-structure compounds represent 37-42 percent in ordinary-regime reforming gasolines, and 20-24 percent in drastic-regime gasolines. The isopentane content is particularly high: 8.7-9.9 percent and 2.5-5.3 percent, respectively. A considerable content of hexane isomers bears noting. Thus, the amount of 3-methylpentane is 5.6 percent in ordinary-regime reforming gasoline, and 2.6 percent in drastic-regime reforming gasoline.

In the C_7 fraction, the content of methylhexanes exhibiting poor operating qualities (octane numbers below 55) represents more than 50 percent of all isoheptanes.

Reforming gasolines contain relatively little C_8, C_9, and C_{10} paraffin hydrocarbons.

Naphthenic hydrocarbons are present in reforming gasolines in smaller amounts: 3-4 percent -- in the ordinary regime, and more than 2 percent -- in the drastic regime.

The composition and structure of aromatic hydrocarbons to a large extent determine the main operating qualities of reforming gasolines. Aromatic hydrocarbons are distributed extremely unevenly in the gasoline (cf. Fig. 1). While the top fraction of reforming gasoline contains no aromatic hydrocarbons at all, their tail fractions contain more than 90 percent.

Among the aromatic hydrocarbons, there is relatively little benzene (less than 2.6 percent) in reforming gasolines. The most valuable hydrocarbons -- toluene -- is present in amounts up to 9 percent in ordinary-regime reforming gasolines, and up to 20 percent in drastic-regime reforming gasolines. There are more high-boiling aromatic hydrocarbons in drastic-regime reforming gasolines than in ordinary-regime reforming gasolines.

Not only reforming gasolines, but also their fractions are used as components in automotive gasolines. For example, when toluene is made from reforming gasoline, the corresponding fraction is isolated, and the top and tail fractions are used as automotive gasoline components. Naturally, the chemical composition of these components can be considerably modified depending on the processing goals.

Other gasoline components. To improve the quality of commercial automotive gasolines, components prepared by polymerization, alkylation, and isomerization of light hydrocarbons are used.

Polymerization can be carried ou without a catalyst (thermal polymerization) and in the presence of acidic catalysts (catalytic polymerization). Olefinic hydrocarbons containing two-five carbon atoms undergo polymerization to produce automotive gasoline components.

In catalytic polymerization conditions, isobutylene reacts most readily, followed by n-butylenes, propylenes, and most slowly of all, ethylene. The feed for industrial catalytic polymerization units consists of the C_3 and C_4 hydrocarbon fractions containing propylenes and butylenes. Propane-propylene and butane-butylene fractions of gases from thermal and catalytic cracking, cooking, pyrolysis, and other processes can undergo polymerization jointly or separately. Usually sulfuric or phosphoric acid is the catalyst.

The composition of polymerization products is extremely inconstant, varies within very wide limits, and depends on the composition of the feed, the catalyst used, and the process conditions.

The product of the polymerization of the broad $C_3 - C_4$ fraction containing from 20 to 40-45 percent olefins is called polymer gasoline. Polymer gasoline is a complex mixture, consisting mainly of unsaturated hydrocarbons. Based on the composition of the feed, it can be assumed that as a result of dimerization alone it can contain more than 30 hexenes, heptenes, and octenes of various structures [46].

In the selective polymerization of the butane-butylene fraction, diisobutylenes are formed, which can be transformed into a mixture of isooctane via hydrogenation. This process was used until recently to produce so-called "technical isooctane." The composition and properties of this product depend on the purity of the butane-butylene fraction.

The reaction of alkylation of paraffin and aromatic hydrocarbons using olefins is also employed to produce high-octane components.

The advantage of alkylation of paraffinic hydrocarbons by olefins compared with the combination of polymerization and subsequent hydrogenation of the dimer is that by means of the single-stage process it is possible to bring to completion the reaction not only with all butylenes contained in the feed, but also with propylenes and amylenes; here it is possible to convert isobutylenes to a high-grade component of automotive gasoline [61].

Alkylation of paraffinic hydrocarbons with olefins can be conducted either thermally or catalytically. Thermal alkylation has not gained wide industrial acceptance owing to the low selectivity of the process and the necessity for cumbersome equipment (high temperatures and pressures)*.

Catalytic alkylation requires milder conditions than thermal. Many compounds have been proposed as catalysts, but only sulfuric acid and hydrogen fluoride have gained extensive industrial use.

The main feed for modern alkylation facilities is the butane-butylene fraction. The overall product of alkylation -- the alkylate -- is an extremely valuable component of automotive gasolines. When the broad faction of olefinic hydrocarbons is used for alkylation, the resulting product sometimes is called alkyl-gasoline.

In the presence of the above-indicated catalysts, besides alkylation polymerization and several other side reactions occur, therefore the composition of alkylates includes hydrocarbons of the most diverse structure in which the number of carbon atoms vary from 5 to 10. The C_5 fraction contains 8-10 percent isopentane and some n-pentane. The C_6 and C_7 fractions have a predominance of hydrocarbons with two methyl groups, and the C_8 and C_9 fractions contain a predominance of hydrocarbons with three methyl groups.

Alkylation of aromatic hydrocarbons with olefins in industrial conditions is carried out catalytically in the presence of aluminum chloride, sulfuric acid, or phosphoric acid and other compounds. The products of alkylation of benzene and its homologs with olefins -- alkylbenzenes -- have good knock resistance, but at the present time they are used used only to a very limited extent as a high-octane component in automotive gasolines. Alkylbenzenes, and also ethylbenzene and isopropylbenzene (cumene) prepared by alkylation of benzene with ethylene and propylene are used in preparing aviation gasolines and in the organic synthesis industry.

The process of isomerization is used to increase the knock resistance of the lightest paraffinic hydrocarbons and to produce isobutane and isopentane in the organic synthesis industry.

Isomerization of light paraffinic hydrocarbons to improve their antiknock properties is carried out in the presence of catalysts such as platinum, palladium, tungsten sulfide, and so on. Isomerization proceeds usually quite profoundly. Thus, in the isomerization of hexane fraction containing 50 percent n-hexane and 10 percent dimethylbutane, a product consisting of 50 percent dimethylbutane and 10 percent n-hexane is produced [49].

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* A high-octane component -- neohexanes -- was once produced by the thermal alkylation of isobutane using ethylene.

By blending light isocomponents with other fractions and with heavy catalytic reforming gasolines, high-octane gasolines with optimal fractional composition can be obtained [62, 64].

Nonpetroleum-origin gasolines. Petroleum is the main feed for the production of automotive gasolines in all countries. Even in countries where the petroleum stocks are low (GDR, FRG, and Japan), automotive gasolines are a product of petroleum origin; petroleum and gasoline are imported. However, in several regions far-removed from oil fields, but where there are large amounts of solid fossil fuels, gasoline is prepared from them.

If solid fossil fuels serve as the feed, automotive gasolines are prepared from their coking or semicoking tars. However the gasoline fraction of these tars contains large amounts of easily oxidized hydrocarbons and nonhydrocarbon impurities and it cannot be used in pure form as a commercial product or as its component. This fraction undergoes special purification, for example with activated clay, sulfuric acid, and so on. It is precisely in this way that automotive gasoline is prepared from oil shale in the Estonian SSR. "Green" shale gasoline contains about 60 percent olefinic hydrocarbons and much phenols, neutral oxygen-containing compounds, and sulfur compounds [65, 66].

After purification, more than 50 percent unsaturated hydrocarbons, 11-15 percent aromatic hydrocarbons, 1-2 percent neutral oxygen-containing compounds, and 24-35 percent naphthenic and paraffinic hydrocarbons remain in the gasoline. These gasolines have an octane number of 65-70.

Gasolines of higher quality are prepared by destructive hydrogenation of the primary semicoking tar from solid fossil fuels [67].

Industrial production of liquid fuels from nonhydrocarbon gases is carried out by means of the so-called synthine process. The crude for this process is a mixture of carbon monoxide and hydrogen. The gasoline fraction of the synthesis product, sometimes called synthine, consists mainly of paraffinic and olefinic hydrocarbons of normal structure. In the olefin hydrocarbons the double bond lies predominantly at the end of the chain, which renders them resistant to oxidation. Nonetheless, owing to the low anti-knock qualities, this gasoline has very limited use.

Nonhydrocarbon Impurities

Gasolines of petroleum origin contain 97-99 percent hydrocarbons; the remainer is accounted for by compounds whose composition includes other elements besides carbon and hydrogen. The main nonhydrocarbon constituents of gasolines are sulfur, nitrogen, and oxygen-containing compounds. In spite of the fact that they are relatively low in content, they very strongly affect the operating qualities of gasolines. Compounds containing sulfur have the greatest influence.

Sulfur compounds. Interest in studying petroleum sulfur compounds has sharpened particularly in recent years since the proportion of sulfur and high-sulfur crudes in total crude oil recovery is rising. Purifying petroleum products from sulfur requires additional means and special installations, and this significantly increases product cost.

Compounds of bivalent sulfur and free (elemental) sulfur predominate in gasolines; of the organic compounds, the mercaptans, sulfides, disulfides, and cyclic (thiophan, thiophene, and their derivatives) are present.

Elemental sulfur dissolves in hydrocarbons in small amounts. It is marked by high reactivity, especially with respect to nonferrous metals -- principally, copper and its alloys. In the presence even of small amounts of sulfur (0.001 percent), these metals blacken, being covered with a film of the sulfides of copper [68].

Hydrogen sulfide (H_2S) is also reactive and dissolves easily in hydrocarbons, and poorly in water [68]. Hydrogen sulfide is corrosive both with respect to ferrous and nonferrous metals.

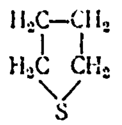
Mercaptans refer to organic sulfur compounds containing a SH group. Most mercaptans are extremely unpleasant and have a sharp odor. Even in very small amounts, they give gasolines a strong and persistent odor.

Low-molecular mercaptans, in ordinary temperatures, are capable of reacting with metals, forming mercaptides. Mercaptans readily dissolve in organic solvents and have weakly pronounced acidic properties. The solubility of mercaptans in water decreases with increase in the molecular weight. The presence of mercaptans in gasoline increases its corrosiveness, degrades its stability, and leads to the formation of gums, deposits, and so on.

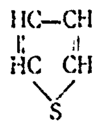
Sulfides are compounds containing a sulfur atom connected to two hydrocarbon radicals. On analogy with ethers, sulfides are sometimes called thioethers. These are neutral, water-insoluble, compounds. At ordinary temperatures sulfides are low in chemical activity.

Disulfides (dithioethers) contain two sulfur atoms located side by side, connected to two hydrocarbon radicals. These are neutral, chemically weakly active compounds with an unpleasant odor.

Thiophans and thiophenes are cyclic compounds:



thiophan



thiophene

Thiophans are colorless liquids with unpleasant odor; they are insoluble in water and at ordinary temperatures are chemically inactive and very stable. Thiophenes are odorless, insoluble in water, and also inactive at ordinary temperatures. These compounds are not corrosive.

Residual sulfur* refers to all other sulfur compounds, whose structure has not yet been established: polysulfides, polyring heterocyclic compounds, sulfones, sulfoxides, alkylsulfoacids, and so on. The properties of compounds differ widely; and the effect of residual structure on the operating properties of gasolines has thus far been little studied.

As to effects on the operating qualities of gasoline, all the sulfur compounds are conventionally divided into compounds of active and inactive sulfur. Active-sulfur compounds include elemental sulfur, hydrogen sulfide, and the mercaptans. All the rest are classified as inactive-sulfur compounds. This division is based on the fact that elemental sulfur, hydrogen sulfide, and mercaptans react with metals and alloys even at ordinary temperatures. Active-sulfur compounds are capable of corroding the metals of tank walls, pipes, fuel feed system parts, that is, all metals (as a rule), with which gasolines current contact during storage and use.

It must be noted that all inactive-sulfur compounds which are present in gasolines are also harmful, for example, for the engine, since all sulfur compounds, on burning, cause increased wear on engine parts, promote the formation of a solid abrasive deposit, and reduce the knock resistance of gasolines, and so on.

The amount of sulfur compounds present in gasoline and their composition depend on the crude and on the gasoline production method [69-70]. The composition of sulfur compounds in gasoline fractions prepared by various crude oil refining processes can differ widely (Table 6).

As a rule, products of the straight distillation of crude oil are somewhat richer in mercaptans and disulfides, while in secondary-origin gasolines a considerable portion of the sulfide compounds are classified as residual-sulfur compound (cf. Table 6).

For the proper use of gasolines prepared from sulfur-containing crudes, in addition to the content of the sulfur compound group, one must know the individual composition of these compounds. The isolation and identification of sulfur compounds began systematically only in the last 15-20 years. Whereas before 1950 the presence of only 20 individual representatives of organic sulfur compounds were established in gasolines, at the present time the number of sulfur compounds identified and isolated in gasolines exceeds 100.

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* This term has been borrowed from analytical practice, and in spite of the fact that it can scarcely be regarded as apt, it is widely used.

Table 6. Distribution of Sulfur Compounds (in Percent of Total Sulfur Content) in Gasolines of Various Origin [10, 71-73]

Бензин 1	Общее содержание серы, % 2	Сероводород 3	Элементарная сера 4	Меркаптаны 5	Сульфиды 6	Дисульфиды 7	Остаточная сера 8
Прямой перегонки 9							
туймазинской девонской нефти 10	0,086	10,5	3,5	22,1	36,0	9,3	18,6
ишимбаевской нефти 11	0,795	16,1	3,5	26,4	27,4	9,2	17,4
бугурусланской нефти 12	0,920	2,2	3,6	5,8	22,7	17,6	48,1
сызранской нефти 13	0,184	5,5	13,5	39,5	1,1	1,5	38,9
орегонской нефти 14	0,217	0,0	6,0	1,4	73,2	11,1	8,3
15 Термического крекинга мазута							
туймазинской нефти 16	0,126	4,0	2,4	4,8	9,6	3,2	76,8
орегонской нефти 17	0,704	0,0	0,0	3,3	1,0	0,5	95,2
Каталитического крекинга фракции 350—450° С туймазинской нефти 18	0,185	0,0	4,9	3,8	14,1	5,4	71,8

Key:
1 -- Gasoline
2 -- Total sulfur content
3 -- Hydrogen sulfide
4 -- Elemental sulfur
5 -- Mercaptans
6 -- Sulfides
7 -- Disulfides
8 -- Residual sulfur
9 -- Straight-run
10 -- Tuymazy Devonian crude
11 -- Ishimbay crude
12 -- Buguruslan crude
13 -- Syzran crude
14 -- Oregon crude
15 -- From thermal cracking of mazut
16 -- Tuymazy crude
17 -- Oregon crude
18 -- From catalytic cracking of 350-450° C fraction of Tuymazy crude

In spite of the diversity of compounds and their varied effect on operating properties, in technical conditions restrictions are imposed thus far on gasolines only with respect to the overall sulfur content; the structure of sulfur compounds or their origin in any particular class have not been made concrete [84-87].

Nitrogen-containing compounds are contained in gasolines in much smaller amounts than are sulfur compounds. Interest in them has appeared only recently in connection with the detection of their influence on the chemical stability of gasolines and the efficiency of additives.

Nitrogen-containing compounds enter gasoline from crudes during refining. The nitrogen content in crudes is 0.3-0.5 percent, corresponding to 2-4 percent nitrogen compounds. But high-tar crudes can contain up to 10 percent nitrogen compounds. However, most nitrogen compounds are concentrated in the heavy fractions of crude and in the residual products.

Thus, in a study of two Central Asian crudes [84], no nitrogen was found in fractions boiling to 150° C; the nitrogen content in fractions up to 230° C did not exceed 0.05 percent of the total nitrogen contained in the crude. Nitrogen also was not detected in straight-run gasoline made from Romashkinskaya crude [82]. And light gasoline made from Devonian crude from the Tuymazy oil field contains 0.022 percent nitrogen [83, page 201].

Compounds of nitrogen in petroleum, in contrast to sulfur compounds, have considerably greater thermal stability and even in secondary petroleum refining processes as a rule are not subject to breakdown and do not pass into lighter fractions. Therefore cracking and reforming gasolines contain just as little nitrogen compounds as straight-run gasolines [88]. For example, catalytic cracking gasoline from vacuum gas oil of Tuymazy crude contains 0.02 percent nitrogen, while straight-run gasoline from this same crude contains 0.025 percent nitrogen. Thus, commercial automotive gasolines have either no nitrogen compounds at all or contain them in very small amounts.

The content of nitrogen compounds in gasoline fractions produced by thermal refining of solid fossil fuels is considerably higher than in gasolines prepared from crude. Their content is especially high in shale gasolines. For example, in the 67-213° C fraction prepared from the tar of Colorado shale, the content of total nitrogen is 1.21 percent, which represents 10-12 percent nitrogen compounds [68].

Oxygen-containing compounds are present in virtually all gasolines, regardless of their origin, but in very small amounts. Gasoline fractions of secondary origin contain usually somewhat more oxygen compounds than straight-run gasolines. All oxygen-containing compounds in gasolines can be provisionally subdivided by their origin into two groups:

those entering gasoline directly from the crude or formed during the production of the gasoline fractions; and

those forming as the result of the oxidation of unstable components of gasoline during storage, transportation, and use.

Here we consider only compounds of the first group; compounds in the second group will be analyzed below when we discuss the chemical stability of gasolines.

All oxygen-containing compounds present in freshly produced gasoline fractions can be divided into acidic -- which are extracted with an alkali solution, and neutral. Acidic compounds, in turn, are subdivided into carboxylic acids and phenols.

Carboxylic acids include compounds characterized by containing a carboxylic group (-COOH) and an aliphatic, aromatic, or naphthenic radical. Work by Academician N. D. Zelinskiy established that acids containing derivatives of naphthenic hydrocarbons and, in particular, cyclopentanes, predominate in petroleum and petroleum products.

These compounds, with the general formula $C_nH_{2n-1}COOH$ or, which amounts to the same thing, $C_nH_{2n-2}O_2$, are called naphthenic acids. The carboxyl group in the early all naphthenic acids is not directly connected to the ring, but is separated from it by one or more methylene groups [6].

In addition to naphthenic acids, fatty acids are also found in gasolines. The lower fatty acids, formic and acetic, have been detected in cracking products and, obviously, are of secondary origin. In the high-temperature refining of petroleum (200-250° C and higher), high-molecular naphthenic acids are subject to cracking, with formation of acids (including fatty acids) of lower molecular weight. These acids are thermally more stable.

In the presence of catalysts, acid breakdown is accelerated. Unsaturated hydrocarbons, ketones, formic, acidic, and other acids, and compounds typical of the oxidative degradation of organic compounds are formed [68].

Carboxylic acids are capable of corroding many metals and alloys: lead, zinc, tin, and copper. The lower fatty acids exhibit the greatest corrosiveness. With increase in molecular weight of acids, their corrosiveness declines.

To prevent the corrosive action of commercial automotive gasolines on metals of containers and fuel systems, the level of carboxylic acids contained in gasolines is strictly regulated by standard. Gasoline is regarded as unsuitable for use if it has an acidity greater than 3 mg KOH/100 ml. This value roughly corresponds to an carboxylic acid content of about 0.01 percent. Most of the carboxylic acids are removed from the gasoline distillates at oil refineries via alkali wash, followed by water scrubbing. The following acids were isolated from the alkaline water used in the scrubbing of straight-run gasolines: formic, acetic, propionic, n-butyric, isobutyric, isovaleric, n-valeric, and dimethylmaleic [6].

Phenols are characterized by containing one or several hydroxyl groups located directly at the aromatic ring. Phenols are contained in crudes and petroleum products in very slight amounts. Their content in gasolines as a rule does not exceed 10 percent of the total of all acidic compounds extracted with alkali. Cracking gasolines contain more phenols than straight-run gasolines. The phenol content (reconverted to trihydrobenzene, percent) in various gasolines is as follows:

Thermal cracking gasolines	
from Tuymazy crudes	0.107
from Baku crudes	0.068
from Nebit-Dag crudes	0.018
from Tatarsk crudes	0.020
Catalytic cracking gasoline	0.002
Catalytic reforming gasoline	0.003

A large content of phenols (0.25-0.36 percent) was found in thermal cracking gasoline produced from mazut of Ekhabi crude [89]. In this case, no phenols were found either in the crude or in the mazut, which confirmed the secondary origin of phenols through the breakdown of ester compounds contained in the crude. Neither phenols nor esters were found in straight-run gasoline produced from this crude.

There is less phenol in catalytic cracking products than in the corresponding thermal cracking fractions.

The following individual phenols were found in gasoline fractions of various origins: o-, p-, and m-cresols, 1, 2, 3-, 1, 3, 4-, 1, 2, 4-, 1, 4, 2-, and 1, 3, 5-xylenols, o-ethylphenol, and diethylphenol. Phenol was found in cracking gasolines [68, 73, 89].

The aromatic ring imparts acidic properties to phenols; the presence of the hydroxyl group is responsible for the facile oxidizability of phenols and their ability to enter into a condensation reaction.

In gasolines, phenols can have a dual action on operating qualities. Some phenols improve fuel qualities, since they are oxidation inhibitors, however phenols are capable of being oxidized, forming gummy, strongly colored compounds. As a whole, phenols in gasolines must be regarded as undesirable components and their removal in the alkali ash of gasoline components promotes improvement in the quality of commercial automotive gasolines.

Neutral oxygen compounds include alcohols, esters, aldehydes, ketones, as well as compounds with a number of functional groups. The diversity of the chemical composition of neutral acid compounds strongly impedes their study. It is for this very reason that there is very limited information on this problem in literature [68].

Neutral oxygen compounds are present in gasolines in very small amounts and are grouped mainly in the high-boiling fractions. In ordinary conditions these compounds have no decisive effect on gasoline properties, but they can undergo chemical changes and can participate in forming new products that even more markedly affect gasoline properties. Most often, neutral oxygen compounds participate in forming gummy substances, whose accumulation leads to a deterioration in the operating qualities of automotive gasolines.

Studying the makeup of sulfur, nitrogen, and oxygen compounds contained in gasolines and an investigation of their effect on the main operating qualities is a vital task and will unquestionably open up new ways of improving the qualities of modern automotive gasolines.

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CHAPTER TWO

VAPORIZATION AND COMBUSTION OF GASOLINES IN ENGINES

Vaporization and Carburetion

In the previous section we established that two elements -- carbon and hydrogen -- predominate in gasoline composition. Accordingly, in the complete combustion of gasoline mostly carbon dioxide and water will be formed. Based on the elementary combustion reactions

$$H_2 + 1/2O_2 \rightleftarrows H_2O$$
$$C + O_2 \rightleftarrows CO_2$$

we can calculate that 8 kg of oxygen is required for the combustion of 1 kg of hydrogen, and 8/3 kg of oxygen for the combustion of 1 kg of carbon.

Based on data on the elemental composition of gasoline, we can find the amount of oxygen needed for the complete combustion of 1 kg of gasoline by the following formula (in kg/kg):

$$L_0 = \frac{8H + \frac{8}{3}C}{100}$$

where H and C represent the content of hydrogen and carbon in the gasoline, percent.

In calculating the amount of air theoretically required for the complete combustion of 1 kg of gasoline (L_0), the formula becomes:

$$L_0 = \frac{8H + \frac{8}{3}C}{23}$$

If the fuel composition includes some oxygen (for example, when using alcohols as components in commercial fuels), this oxygen participates in combustion and a lesser amount of air is required for the complete combustion of these fuels:

$$L_0 = \frac{8H + \frac{8}{3}C - O}{23}$$

where O is the amount of oxygen present in the fuel, percent.

Usually, in calculations the amount of oxygen and sulfur in commercial automotive fuels is not taken into account.

Commercial automotive gasolines include hydrocarbons in which the carbon to hydrogen ratio can vary widely. For example, 1 kg of butane contains 0.827 kg carbon and 0.173 kg hydrogen, while 1 kg of benzene contains 0.923 kg carbon and only 0.077 kg hydrogen. The theoretically required amount of air for the combustion of butane is 15.5 kg/kg, while only 13.3 kg/kg for the combustion of benzene. The predominance in gasoline of hydrocarbons with a given structure naturally affects the theoretically required amount of air for the combustion of gasoline as a whole (cf. below, Table 9). This factor must be taken into account in making various engine tests, since in recent years the content of aromatic hydrocarbons, especially in high-octane automotive gasolines, has risen appreciably.

To ensure the most complete combustion of a mixture in an extremely short time interval, gasoline must be converted from the liquid state to the vapor state and vapor must be mixed with the required amount of air, that is, a combustible mixture must be produced.

The combustible mixture in internal combustion engines with spark ignition can be formed by two fundamentally different ways. The mixture can be prepared outside the engine cylinder, in a special instrument -- the carburetor, and directly in the engine cylinder, into which air and fuel are separately fed.

The direct injection of fuel into the cylinder cavity, in a special prechamber, or in the air intake manifold is carried out during the intake or compression strokes via a nozzle using a special pump. Less time is expended in vaporizing fuel by means of direct injection. Factors accelerating vaporization include the intensified eddy movement of air and the high temperature within the cylinder.

The method of forming the combustible mixture by direct gasoline injection has several advantages over carburetion. The principal advantages are these: greater uniformity in the distribution of gasoline by engine cylinders and increase in the charge factor and in the liter capacity owing to a reduction in hydraulic drag in the intake system (absence of a carburetor).

Direct injection has found application in several piston type aircraft engines, however until recently this method of carburetion has found limited application in automotive engines.

In recent years interest in direct ignition has again risen, associated with attempts to build a multifuel, or as it is called, a "all-poison" engine based on the spark-ignition engine.

The problem of building an "all-poison" engine, that is, an engine capable of operating on gasoline, kerosene, and diesel fuel, has long engaged the efforts of scientists and designers. The main trend in solving this problem has long reduced to "adapting" the diesel engine to run on gasoline.

At the present time several patterns have been given for direct-ignition engines, spark-ignition engines, and engines with stratified combustion of fuel in eddy air that can use gasoline as well as heavier kinds of fuels [1-5].

A serious disadvantage of direct ignition is the complexity of engine design, therefore the method of forming the combustible mixture by fuel carburetion is most extensively used in automotive engines.

The air flow rate in the carburetor venturi is approximately 20-30 times greater than the air jet flow rate. These conditions the air jet breaks up into fine droplets, whose average diameter is 0.1-0.2 mm. The droplets formed are entrained by the air flow and begin to vaporize intensively. Gradually the droplet velocity increases to values close to the velocity of the air-vapor flow of the combustible mixture; here, in spite of the high turbulence of the flow, their vaporization slows down and some of the droplets can even fall into the engine cylinder, where under the effect of high temperature final vaporization takes place. Thus, in an engine with a steady-state regime gasoline vaporization begins in the carburetor, continues in the intake manifold, and can terminate in the engine cylinders.

As the result of numerous visual observations and photographic recording of the formation of the combustible mixture in a carburetor engine, it was established that some of the droplets on exiting from the carburetor venturi settle on the walls of the intake manifold and form a film of liquid fuel. The air-vapor flow sweeps the film along the walls of the intake manifold toward the engine cylinders. Even if the manifold walls are polished, the film of liquid fluid travels 50-60 times slower than the air-vapor mixture. As the film moves from the wall surface, intense vaporization of gasoline occurs [6].

The presence of the liquid film introduces crumble of substantial complications in the preparation of a homogeneous mixture.

Of greatest significance is the nonuniformity in the distribution of the mixture by engine cylinders; here a flammable mixture of different quality can enter individual cylinders.

There are two kinds of distribution nonuniformity -- quantitative and qualitative.

The quantitative nonuniformity of distribution refers to the difference in the quality of the combustible mixture in individual cylinders with respect to the air excess coefficient. The qualitative nonuniformity of mixture distribution characterizes the different content of individual gasoline or additive fractions in the combustible mixture entering different engine cylinders.

One of the reasons for the nonuniform distribution of the mixture is the following. Owing to the cyclic nature of the admission of the combustible mixture into engine cylinders, the movement of the combustible mixture flow through the intake system is of a pulsing nature. During the intake process, the combustible mixture travels in the direction of the cylinder, and the flowrate of the mixture gradually varies as a function of rarefaction in the cylinder and in the flow-through cross-section in the zone of the intake valve. Closing of the valve prevents access of the mixture into a cylinder. But the mixture flow has certain inertia, and this results in the mixture continuing to enter the given connection of the intake line. The liquid film of fuel on the walls of the line has greater inertia than the air-vapor mixture. Therefore in the deceleration of the flow caused by closing of the intake valve, the liquid film of fuel continues to move toward the cylinder. This produces not only an overall enrichment of the mixture in the given connection of the inlet line, but also the redistribution of fuel along the length of the flow: some of the mixture located directly in the zone of the intake valve proves to be most enriched with fuel. And on arriving at the well-heated zone of the intake valve, the liquid fuel film begins to vaporize intensively [7].

At the first instant after opening of the intake valve, basically fuel-enriched air-vapor mixture located in the zone of the intake valve will enter the cylinder. Along with the air-vapor mixture, into the cylinder would also enter the liquid phase of the fuel accumulating in the zone. Therefore at the very beginning of the intake process a very rich mixture will be in the cylinder. Then the mixture must become somewhat leaned, since after the enriched mixture located in the zone of the intake valve, into the cylinder will begin to flow the air-vapor mixture located in regions of the intake line further removed from the valve. Thus, nonuniformity of mixture distribution by cylinder volume is born [7].

However, when two or more engine cylinders are fed from the same cavity or from a single branched intake manifold, the above-described effects cause the nonuniformity of combustible mixture distribution by engine cylinders.

If two cylinders are fed from a single cavity or from a branch, the enriched mixture, after a pause (cf. above), enters the cylinder in which the intake stroke begins earlier in accordance with the established engine cylinder firing order.

Fig. 2 shows the layout of the intake line and the distribution of the mixture by cylinders of a GAZ-21 engine that has following cylinder firing order: 1-2-4-3. After closing of the intake valve 2 of the cylinder, enrichment of the mixture occurs in the supply connection of the cylinder and also in the overall section of the forward branch of the intake line. The same occurs also in the rear branch of the intake line.

As a result of the uneven distribution of the liquid phase of fuel, enriched mixture enters cylinders 1 and 4, and a lean mixture enters cylinders 2 and 3.

In addition to the effect occurring due to the cyclic admission of the combustible mixture into cylinders, there are several other factors responsible for the nonuniform distribution of the mixture by individual branches and connections of the intake line. Here we include, mainly, design features of the carburetor of its mixing chamber and the intake manifold, whose considerations are beyond the scope of this book [7, 8].

The qualitative nonuniformity of combustible fuel distribution by engine cylinders is associated first of all with the fact that gasolines are a complex mixture of hydrocarbons. The conversion of some gasoline fractions into the vapor state proceeds in a specific order. First the lower-boiling hydrocarbons are vaporized, and then the high-boiling fractions, and the liquid phase is enriched with heavy hydrocarbons boiling at high temperatures.

This fact of fuel fractionation during its vaporization occurs in the preparation of the combustible mixture in the carburetor.

The vaporization of light hydrocarbons from droplets and film leads to enrichment of the air-vapor mixture with low-boiling hydrocarbons, and enrichment of the liquid phase with high-boiling hydrocarbons. Accordingly, in the cylinders where more air-vapor phase arrives an excess of light gasoline fractions will be produced, while in the cylinders where more liquid phase arrives, there will be a predominance of high-boiling, heavy gasoline fractions. Naturally, in the event gasolines containing additives are used, the vaporization of each additive proceeds simultaneously with the gasoline fractions which are close to it involatility the nonuniformity of the distribution of gasoline fractions by cylinders leads also to the nonuniformity of additive distribution. This phenomenon is especially vital in the distribution of antiknock additives by engine cylinders and ensuring the sweeping away of their combustion products (cf. below).

Fig. 3 shows the degree of nonuniformity of hydrocarbon and additive distribution by cylinders as a function of boiling points. As the boiling

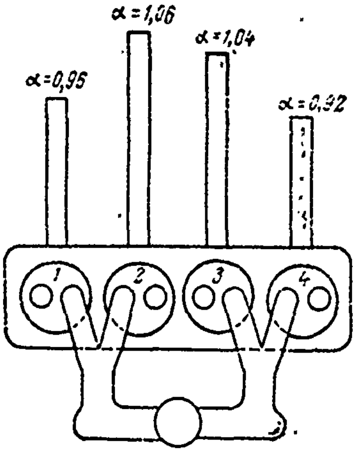

Fig. 2. Distribution of flammable mixture in four-cylinder engine of the GAZ-21 vehicle. Cylinder firing order 1-2-4-3, n = 2000 rpm, and throttle valve fully open [7]

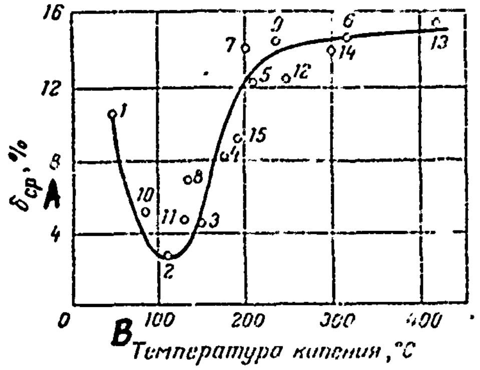

Fig. 3. Dependence of mean degree of distribution nonuniformity of hydrocarbons and additives, δ_{av}, for cylinders of a V-type eight-cylinder engine as a function of their boiling points [7]:

1 -- cyclopentane
2 -- toluene
3 -- xylene
4 -- p-cymene
5 -- tetralin
6 -- p-octadecane
7 -- tetraethyl lead
8 -- ethyltrimethyl lead
9 -- manganese antiknock
10 -- ethylene chloride
11 -- ethylene bromide
12 -- dibromotoluene
13, 14, and 15 -- phosphoric additives

Key: A -- δ_{av} [av = average]
B -- Boiling point

point of a component or additive approaches the boiling point of the mean gasoline fractions, the mean degree of nonuniformity in their distribution by engine cylinders decreases, reaching a minimum at 110-115° C. It is important to know that components and additives boiling above 200° C (the end boiling point of gasoline is 205° C) have virtually little difference in the nonuniformity of distribution by engine cylinders.

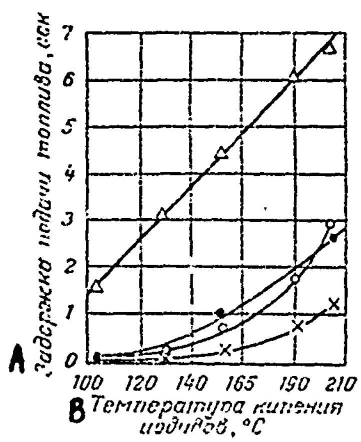

Fig. 4. Effect of boiling point of iodides on their lag in the intake manifold of four different motor motor vehicles [9]

Key: A -- Fuel feed lag, sec
B -- Iodide boiling point

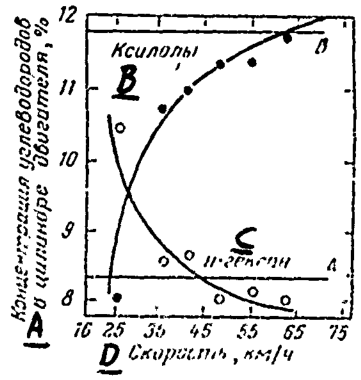

Fig. 5. Dependence of concentration of n-hexane and m- and p-xylenes in a working mixture on velocity during acceleration of the vehicle; throttle valve fully open [9]. Concentrations of hexane and xylenes in the initial fuel are denoted by the lines A and B.

Key: A -- Concentration of hydrocarbons in engine cylinder
B -- Xylenes
C -- n-hexane
D -- Velocity, km/hr

We have considered several features of mixture distribution by engine cylinders in steady-state regimes. In recent years, the attention of investigators has been drawn to eliminating the qualitative nonuniformity which arises in variable engine operating regimes, in particular, during the acceleration of a motor vehicle.

An increase in the crankshaft rpm of an engine is achieved by opening the throttle valve. This moment especially unfavorable conditions are produced for spreading and vaporization of gasoline, because initially the air flowrate drops sharply and rarefaction in the intake system decreases. Much of the gasoline settles on the walls of the intake manifold, and the air-vapor mixture is considerably increased by low-boiling hydrocarbons, that is, fractionation of gasoline occurs. Immediately after opening of the throttle valve, the air-vapor mixture enters the cylinders since it exhibits considerably less inertia than the liquid film, thus, during some period of time a combustible mixture significantly enriched with the highly volatile low-boiling hydrocarbons arrives in the engine cylinders.

This phenomenon has been studied in four different motor vehicles as they were accelerated with full-open throttle. Alkyl iodides with different boiling points were injected alternately into the intake manifold of each engine. A recording was made of the time required for the iodide to travel from the instant it was injected in the intake line until it reached the end of the intake line where filter paper soaked with starch solution, which turned blue when encountering iodide, was fastened. The results show (Fig. 4) that with increase in the boiling point of an iodide, the delay in the appearance of its combustion products at the end of the intake line increases. The higher the boiling point of the iodide, the more of it enters the liquid film and the more slowly it travels through the intake manifold, the later the products of its decomposition reach the end of the intake manifold [9].

These experiments show that the lag of high-boiling fractions in the intake manifold depends strongly on the design features of an engine, but general correlations are the same for all four vehicles tested [9].

Another interesting experiment was performed on a motor vehicle during tests on a racing drum stand. The engine was operated in acceleration conditions with throttle wide open. No spark was fed to one of the cylinders and from it samples of the mixture were taken upon attainment of six different velocities. The initial gasoline contained approximately 12 percent of a mixture of m- and p-xylenes and about 8 percent n-hexane (Fig. 5, lines A and B). These compounds were readily detected in the samples of the combustible mixture by liquid-gas chromatography.

At low velocities in the initial acceleration period (cf. Fig. 5), the concentration of low-boiling hexane in the mixture is considerably higher than in the initial gasoline, while the concentration of high-boiling xylenes in the mixtures less than in the gasoline. These experiments quite unambiguously demonstrate the fractionating of gasoline in the intake manifold the enrichment of the mixture with low-boiling fractions during the first period after opening of the throttle valve. With increasing acceleration of the vehicle, the nonuniformity in the distribution of the fractions becomes less.

These same experiments show that nonuniformity in the distribution of fraction during acceleration decreases with increase in the initial speed of the vehicle. Intensifying heating of the intake manifold also leads to a decrease in nonuniformity [9].

Besides merely observations of the nonuniformity in the distribution of fraction during acceleration, there are also data dealing with the quantitative aspect of this phenomenon. Special calculations show that in the first period of acceleration of a vehicle fuel entering the cylinders will consist of a mixture of 20 percent general-composition fuel and 80 percent light fractions. The calculation was verified with a vehicle in stand conditions in which samples were taken from a cylinder to which no spark was admitted. The results (A) of the liquid-gas analysis of the samples were compared with the results of the same analysis of a sample prepared in laboratory conditions and consisting of 20 percent general-composition fuel and 80 percent light fractions of this same fuel (B) sampled in the temperature range from the beginning of boiling through 70 percent boiling [9]:

	Amount of components, percent by weight	
	A	B
n-Butane	1.71	5.26
Isopentane	10.29	7.14
n-Pentane	15.72	11.98
2,3-Dimethylbutane	8.38	6.13
3-Methylpentane	6.19	4.24
n-Hexane	13.21	12.71
2,2,3-Trimethylbutane	1.99	1.95
2,3-Dimethylpentane	2.11	2.70
2-Methylhexane	2.95	4.14
Cyclohexane	5.56	8.76
Benzene	3.21	3.14
Toluene	9.86	9.69
Ethylbenzene	1.74	1.97
Xylenes	6.46	6.75
Cumene	0.31	0.34
n-Propylbenzene	0.10	0.29
1-Methyl-4-ethylbenzene	1.34	1.62
1,2,3-Trimethylbenzene	1.12	0.91

These data confirm that the calculation was correct. Some difference in the lightest hydrocarbons is accounted for by the difficulties in their condensation in sampling from the cylinder of the running engine.

Thus, in variable regimes fractionation of fuel takes place, which is especially important for these gasolines in which individual fractions differ widely in properties from the gasoline as a whole. This applies above all to the antiknock qualities of gasolines and their fractions (cf. following section).

After brief familiarization with the preparation of a combustible mixture in the intake system of an engine, let us examine what then are the properties of gasoline and how they affect this process.

Numerous investigations show that the quality of carburetion and uniformity of the distribution of the mixture by engine cylinders depend on such physical properties of the fuel as saturated vapor pressure, fractional composition, latent heat of vaporization, coefficient of vapor diffusion, viscosity, surface tension, heat capacity, and density.

A most important property responsible for the volatility of fuel is its saturated vapor pressure.

We must distinguish between static evaporation in which relative movement of fuel and air along the surface of their contact is absent, and dynamic vaporization occurring in conditions in which vaporizing fuel is "swept" by air with relative movement of fuel and air.

Static vaporization occurs when fuel is stored in tanks. In internal combustion engines dynamic vaporization of fuel takes place. Under otherwise equal conditions, the rate of dynamic vaporization is always higher than the rate of static vaporization for the following reasons.

When fuel vaporizes, its molecules fly off from the liquid into the ambient air. Some of the vaporizing molecules can again collide with the surface of the liquid and be absorbed by it. The degree of vaporization of a fluid is determined by the difference between the number of molecules flying off from the liquid and those absorbed again by it. The intensity or rate of vaporization depends on the initial concentration of the given fuel molecules in the air and on the rate of their diffusion. If the gaseous space over a liquid is unlimited, vaporization occurs at maximum intensity. In this case we have free vaporization. In an enclosed volume, at the outset the rate of vaporization is equal to the rate of free vaporization, but with increasing saturation of the air with fuel molecules the number of molecules returning to the liquid phase rises, and the vaporization process slows down. At a certain concentration of few molecules in the air, the number of molecules flying off from the liquid and returning to it becomes equalized, and a state of dynamic equilibrium is attained [10].

The maximum concentration of fuel vapor in air at which the state of dynamic acceleration is established characterizes the saturated vapor pressure of the given fuel. The higher the saturated vapor of the fuel, the greater the amount of fuel that is vaporized until the concentration of the molecules in the vapor phase reaches the state of dynamic equilibrium.

The vaporization rate of a fuel, according to Dalton's law, is determined by the following equation:

$$v = A(P_{sat} - p) \quad ,$$

where v is the rate of vaporization of the fuel; p is the partial pressure of the fuel vapor in the air of the surface of the fuel; and A is the coefficient of proportionality dependent on vaporization surface area,

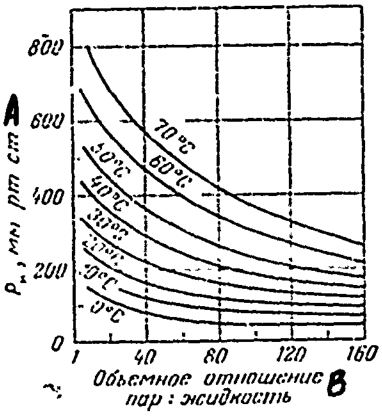

Fig. 6. Dependence of saturated vapor pressure of gasoline on volumetric ratio of vapor and liquid phases at several temperatures

Key: A — P_{sat} [sat = saturated], mm Hg
B — Volumetric ratio vapor:liquid

total pressure, coefficient of fuel vapor diffusion in the ambient medium, and so on.

Thus, the saturated vapor pressure of fuel is the most important indicator determining its vaporizability in the intake manifold of an engine.

The saturated fuel vapor pressure is a function of its composition and depends on the temperature and ratio of the vapor and liquid phases.

Saturated vapor pressure in laboratory conditions is customarily determined in two ways. The first method, the Reid method (GOST 1756-52), consists in recording on a manometer the saturated vapor pressure of gasoline placed in a special bomb and heated in a water bath to 38° C. The ratio of the volumes of a liquid and vapor phases in the Reid bomb is 1:4.

The second method, developed by Valyavskiy and Budarov (GOST 6668-53), consists in determining the change in the volume of the air-vapor mixture when the gasoline is heated to 38° C in a glass instrument. The ratio of the liquid and vapor phase volumes for determination by the Valyavskiy-Budarov method is taken as 1:1.

All of the methods of determining the saturated vapor pressure of fuels (the Sorrel-NATI [State All-Union Scientific Research Institute of Tractors] method, in the Campbell bomb, the method of lower of mercury in a glass tube, and so on) have no gained wide acceptance in view of low precision or cumbersome equipment [11].

In recent years, a micromethod of determining the saturated vapor pressure of gasoline, developed by the ESSO Company (a phase ratio of 4:1) and the General Motors method (phase ratio of 25:1) have been used in foreign practice.

The fuel ratio, when determining the saturated vapor pressure. has a very strong influence on the results.

When the volume of the vapor phase compared with the volume of the liquid phase is not large, the amount of readily volatile hydrocarbons contained in gasoline will prove to be sufficient to saturate the vapor phase. In this case, at saturation the composition of the liquid phase remains practically unchanged, and at equilibrium vapor and gasoline of the initial composition coexist.

When the volume of the vapor phase considerably exceeds the volume of the liquid phase, already a considerable amount of easily volatile hydrocarbons is expended for saturation; here the compensation of the liquid phase changes. In the saturation state, the vapor phase is in equilibrium with a liquid of a now modified composition. The saturated vapor pressure in this case differs from the saturated vapor determined for a small volume of the vapor phase. In other words, with an increase in the ratio of vapor phase to liquid phase, the saturated vapor pressure found will be reduced (Fig. 6). Accordingly, the pressure values obtained by the Reid method are usually 60-80 mm Hg below the values determined by the Valyavskiy-Budarov method. The effect of the phase ratios on the saturated vapor pressure determined increases with increase of the determination temperature (cf. Fig. 6).

It must be noted that in natural conditions in an engine the ratio of the vapor to the liquid phase in conditions when the gasoline vaporizes in the intake manifold varies within very wide limits. In a heated engine, in steady-state operating conditions, this ratio is very large, which can be demonstrated by calculation. Complete combustion of 1 g of gasoline is caused by 15 g of air, which occupies an volume at 20° C and 760 mm Hg of 12,500 cm^3. This volume of air can be taken as the volume of the air-vapor space into which fuel vaporizes in the intake manifold of an engine. With the volume of the liquid phase equal to the volume of 1 g gasoline at 1.33 cm^3, the ratio of the vapor to the liquid phase will be about 9500. If we take into account the reduction in the volume of liquid phase with increasing vaporization, we must consider that in conditions of a steady-state regime in a warmed engine the phase ratio is more than

10,000 and even for operation with rich mixtures the air-fuel mixture is far from saturation [6].

On the other hand, during the first period of starting, for ignition to appear in the cylinders of a carburetor engine, a mixture with an excess air coefficient in the limits 0.05-0.07 must be supplied. Therefore, during this period vaporization of gasoline will proceed at a phase ratio of 500-700. These values of the phase ratio are obviously minimum for an engine, but they also are quite large and afford the conclusion that in all possible regimes vaporization of gasoline in an engine occurs at high ratios of vapor to liquid phase -- from 500 to 10,000 and higher. Vaporization of the gasoline in the engine always occurs in a medium that is far-removed from saturation. From this point of view data on the saturated vapor ratio of gasoline determined by presently adopted methods (phase ratios of 4:1 and 1:1) used in evaluating the volatility of fuels in the intake system of an engine are of important, but still not absolute significance. This is associated, first of all, with the difference in the fuel vaporization conditions in laboratory methods and in actual engines.

The saturated vapor pressure of a hydrocarbon with a specific structure and of a fuel with a specific composition depends on temperature. The nature of this dependence can be seen in Fig. 7, where the data on the saturated vapor pressure at different pressures are given for several domestic automotive gasolines [12, 13].

Using the Clausius-Clapeyron equation, we can represent the saturated vapor pressure of gasoline as a linear dependence on temperature in semi-logarithmic coordinates [6]

$$\lg P_{sat} = -A/T + B$$

where T is the absolute temperature; and A and B are constants.

The saturated vapor pressure at below-zero temperatures is vital for the determination of the starting qualities of gasolines (cf. text page 183 [translation page 230]).

When examining the vaporization rate of fuel, it was noted that the coefficient of proportionality in the formula of Dalton's law depends on the diffusion coefficient of fuel vapor into the ambient atmosphere.

As a result of diffusion, the concentration of vaporizing molecules above the fuel surface decreases and new fuel molecules evaporate. The higher the diffusion rate of fuel vapor, the more rapidly the fuel vaporizes. The diffusion rate of vapor, according to Fick's law, is proportional to the concentration gradient of the diffusing compound

$$w_D = D\frac{dc}{dx}$$

where w_D is the diffusion rate or the diffusion flow;

D is the coefficient of diffusion; and dc/dx is the concentration gradient. The diffusion coefficient depends on the temperature and the ambient pressure

$$D = D_0\left(\frac{T}{T_0}\right)^m\frac{P_0}{P}$$

where $m = 1.5$-2.0 (on the average, $m = 1.7$); P_0, P, T_0, and T are the initial and end pressures and temperatures.

The diffusion coefficient increases with temperature, and decreases with increase in pressure.

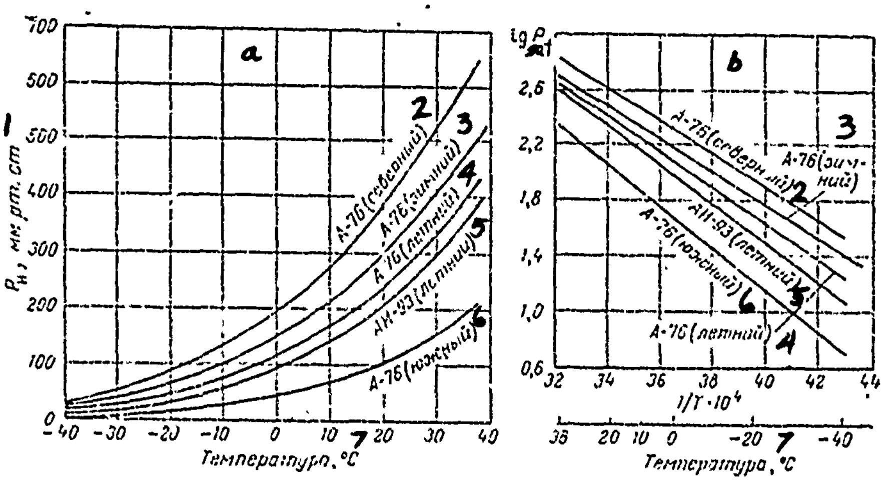

Fig. 7. Dependence of P_{sat} of gasoline on temperature

a -- in usual coordinates
b -- in semilogarithmic coordinates
Key: 1 -- P_{sat}, mm Hg
2 -- A-76 (northern)
3 -- A-76 (winter)
4 -- A-76 (summer)
5 -- AI-93 (summer)
6 -- A-76 (southern)
7 -- Temperature

Table 7. Diffusion coefficient in cm^2/sec of vapor of hydrocarbons and their mixtures in air at atmospheric pressure and various temperatures [6]

Углеводород или топливо 1	10° C	20° C	30° C	40° C
н-Гептан 2	0,0673	0,0736	0,0797	0,0856
Циклогексан 3	0,0696	0,0745	0,0781	0,0829
Метилциклогексан 4	0,0571	0,0615	0,0660	0,0706
Бензол 5	0,0834	0,0900	0,0920	0,0993
Бензин каталитического крекинга 6	0,0841	0,0902	0,0960	0,1002
Бензин прямой перегонки 7	0,0847	0,0910	0,0974	0,1011
Средние величины для бензинов 8	0,0845	0,091	0,097	0,102

Key: 1 -- Hydrocarbon or fuel
2 -- n-Heptane
3 -- Cyclohexane
4 -- Methylcyclohexane
5 -- Benzene
6 -- Catalytic cracking gasoline
7 -- Straight-run gasoline
8 -- Mean values for gasolines

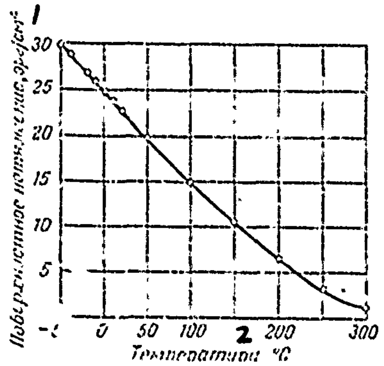

Fig. 8. Dependence of surface tension of gasoline on temperature

Key: 1 -- Surface tension, erg/cm^2
2 -- Temperature, ° C

Values of the diffusion coefficient of vapor in air are given in Table 7 for several individual hydrocarbons and gasolines. Since the diffusion coefficients of gasolines of various origins are quite similar, the table also gives the mean data for gasolines that can be used in the calculations.

Strictly speaking, the term diffusion refers to the propagation of matter in some medium caused by the nonuniformity of its concentration in the medium, occurring only due to the thermal motion of the molecules in the absence of convection (mixing currents) [14]. However, to evaluate the vaporization of gasoline in an intake manifold, the diffusion coefficient is also determined at various air flow rates. It was established that the diffusion of gasoline vapor in still air is less than in moving air.

Air flowrate, m/sec	Diffusion coefficient, cm²/sec
0 (15° C)	0,09
10 (15° C)	0,166
80 (15° C)	0,420
0 (100° C)	0,146
10 (100° C)	0,268
80 (100° C)	0,682

[Commas indicate decimal points.]

By Dalton's law, the evaporation rate of liquids is directly proportional to the surface tension. For the evaporation of gasoline in the intake system of an engine, surface tension depends on the fineness of the spray. The fineness of the spray depends both on the conditions of atomization (the size and shape of the spray nozzle opening and the air flowrate in the venturi), as well as on the properties of the fuel, and above all on surface tension.

In approximate terms, it is customary to assume that as gasoline flows from a constant-section nozzle, the mean radius of droplets is directly proportional to surface tension:

$$r = 0{,}4g\,\frac{\sigma}{v^2}$$

where r is the mean radius of the droplets; g is acceleration due to gravity; σ is the surface tension; and v is the air flowrate in the venturi.

Surface tension characterizes the condition of the surface of a liquid; if it is numerically characterized by the work that must be done to form a unit area of surface. This work is expended in overcoming the attractive forces between molecules as they exit into the surface layer. The surface tension of hydrocarbons depends on their structure. Paraffinic hydrocarbons, boiling in the range 65-300° C, have a surface tension in the range 18-28 erg/cm^2, while it is somewhat higher for naphthenic hydrocarbons — 22-29 erg/cm^2; and for aromatic hydrocarbons, it is even higher yet — 28-32 erg/cm^2. The surface tension for automotive gasolines is 20-24 erg/cm^2.

The surface tension of individual hydrocarbons and of motor fuels with specific gravity ρ_4^{20} in the range of 0.60 to 0.92 at 20° C can be calculated by the following empirical formula:

$$\sigma = 50\rho_4^{20} - 15{,}0$$

Calculated data based on this formula agree quite satisfactorily with experimental results.

We have spoken of surface tension of hydrocarbons and fuel at the interface with air. At the interface with other media, the surface tension can differ appreciably. In particular, the surface tension of gasolines at the interface with water is 47-50 erg/cm^2.

With increase in temperature, the surface tension of hydrocarbons and automotive fuels decreases and becomes equal to zero at the critical temperature [15]. The nature of the change in surface as a function of temperature is depicted in Fig. 8.

In the temperature range that is sufficiently removed from the critical point, variation in surface tension with temperature can be assumed to be linear and the following formula may be used:

$$\sigma_t = \sigma_0 - \alpha t$$

where α is an empirical coefficient, which is 0.1 for hydrocarbon fuels.

The vaporization of fuels of varied origins is strongly affected by their heat of vaporization.

If it is assumed that the vaporization of a fuel in the intake system of an engine proceeds adiabatically, all the required amount of heat Q(kcal) can be abstracted from the air in which the vaporization occurs, or from the fuel itself, that is,

$$Q = Q_a + Q_f \quad [a = \text{air},\ f = \text{fuel}]$$

Air and fuel in this case are cooled from t_0 to the final temperature of the resulting mixture t.

When 1 kg of fuel passes into an engine, an amount of heat equal to the heat of vaporization r must be expended for its complete vaporization. Actually, all the fuel is not vaporized, but some part of it -- x. Here αL_0 is the amount of air passes through the intake system, where α is the excess air coefficient and L_0 is the theoretically required amount of air. Then individual components of the heat balance in the intake system will appear as follows:

$$Q = xr$$

$$Q_f = c_f(t_0 - t)$$

$$Q_a = \alpha L_0 c_a(t_0 - t)$$

where c_f is the heat capacity of liquid fuel and c_a is the heat capacity of air at constant pressure.

Hence it follows that

$$xr = Q_f + Q_a = c_f(t_0 - t) + \alpha L_0 c_a(t_0 - t)$$

and the temperature drop in the intake manifold is

$$t_0 - t = (xr/(\alpha L_0 c_a + c_f)).$$

Thus, the decrease in temperature in the vaporization of the fuel in the intake system is determined by the heat of vaporization r, the composition of the combustible mixture αL_0, and the heat capacity of the fuel c_f (Table 8).

Calculations show that the temperature drop of the mixture in the intake manifold is most strongly affected by the heat of vaporization.

For individual hydrocarbons and automotive fuels, the heat of vaporization decreases with increase in the molecular weight and in the boiling point. But at the same molecular weight of hydrocarbons, the largest heats of vaporization are found for aromatic and acetylene hydrocarbons, and the smallest for paraffinic and olefinic; naphthenic hydrocarbons are intermediate in value. Hydrocarbons of isomeric structure in each class have a lower heat of vaporization and the normal-structure hydrocarbons [14].

Among the compounds that have found use as automotive fuel components, alcohols have a highest heat of vaporization. The temperature decrease in the intake manifold owing to the higher heat of vaporization of alcohols

Table 8. Effect of physicochemical properties on the temperature drop in the intake manifold ($\alpha = 1$)

Углеводород или топливо 1	Теплота испарения, ккал/кг 2	Теплоемкость, ккал/(кг·град) 3	Снижение температуры смеси при полном испарении топлива, °C 4
Изопентан 5	82,0	0,52	19,5
н-Гептан 6	75,8	0,52	18,3
Изооктан 7	65,1	0,47	16,0
Бензол 8	94,2	0,40	26,4
Изопропилбензол 9	75,5	0,41	20.3
Метиловый спирт 10	263,4	0,58	123,1
Этиловый спирт 11	219.5	0,57	80,4
Диэтиловый эфир 12	86.2	0,51	26,3
Бензины 13			
А-66	69.0	0,49	16,8
Б-70 14	75.0	0,50	18,1
А-76	71,0	0,48	17,7
АИ-93 15	73,0	0 47	18,6
Керосин 16	52,0	0,46	13,3

Key: 1 -- Hydrocarbon or fuel
2 -- Heat of vaporization, kcal/kg
3 -- Heat capacity, kcal/(kg·deg)
4 -- Drop in mixture temperature in the total vaporization of fuel
5 -- Isopentane
6 -- n-Heptane
7 -- Isooctane
8 -- Benzene
9 -- Isopropylbenzene
10 -- Methyl alcohol
11 -- Ethyl alcohol
12 -- Diethylester
13 -- Gasolines
14 -- B-70
15 -- AI-93
16 -- Kerosene

is approximately three times greater than in the vaporization of hydrocarbon fuels. However, the actual temperature drop when alcohols vaporizing in an engine is even greater, since less air is required for the combustion and for hydrocarbon fuels (cf. Table 9).

This property of alcohols is widely used in their employment as fuels for racing motorcycles and automobiles. The thermal regime of the engines in these vehicles proves to be usually highly stressed and the use of alcohols makes it possible to lower the temperature of gases at the end of the intake stroke.

The lower temperature of the mixture at the end of the intake when alcohols are used leads to an increase in the density of the charge and a higher charge factor, which in turn leads to an increase in the mean effective pressure and an increase in the engine power output.

The role of heat capacity of fuel in reducing the temperature during vaporization is relatively minor; furthermore, the actual heat capacities of different fuels are quite similar.

The heat capacity of liquid hydrocarbons and automotive fuels at 0° C varies within the range 0.60 - 0.35 kcal/(kg·deg). Paraffinic hydrocarbons have higher heat capacities than aromatic and naphthenic. Normal-structure hydrocarbons exhibit greater heat capacity than isomeric. The heat capacity of fuels as a rule decreases with increase in density [14].

The heat capacity of liquid hydrocarbon fuels at 0° C can be calculated by the empirical formula:

$$c_f = \frac{A}{\sqrt{\rho_4^{15}}}$$

where A is a coefficient, 0.42 for paraffinic hydrocarbons and 0.37 for aromatic, and 0.403 for motor fuels, including gasolines.

Calculated heat capacities based on this formula differ by no more than 4 percent from experimental values [14].

The dependence of the heat capacity of liquid hydrocarbons and automotive fuels on temperature for a relatively narrow temperature range can be assumed to be linear and can be calculated by the formula

$$c_f = c_{f_0}(1 + \alpha t),$$

where α is a coefficient, which is 0.001 in the temperature range 0 - 200° C.

It must be noted that as a result of a decrease in temperature in the intake manifold, the fuel vaporization conditions are deteriorated. Therefore, in modern automotive engines the intake manifolds are heated.

The physical properties of gasoline affect also the consumption of fuel through the calibrated orifices in the carburetor. In this case, the viscosity and specific gravity of gasoline are of the greatest importance.

Automotive gasolines have relatively low viscosities:

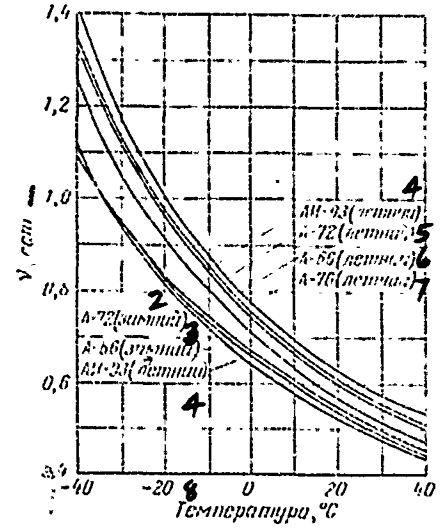

Fig. 9. Dependence of kinematic viscosity of gasolines on temperature

Key: 1 -- Centistokes
2 -- A-72 (winter)
3 -- A-66 (winter)
4 -- AI-93 (summer)
5 -- A-72 (summer)
6 -- A-66 (summer)
7 -- A-76 (summer)

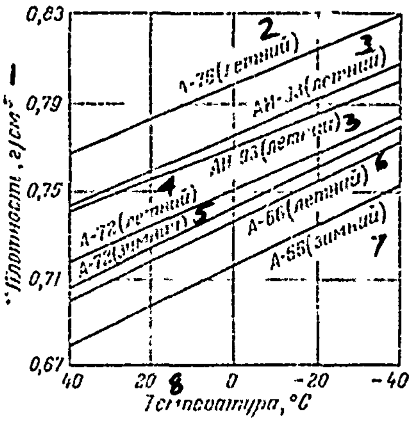

Fig. 10. Temperature dependence of the specific gravity of gasolines

Key: 1 -- Density, g/cm^3
2 -- A-76 (summer)
3 -- AI-93 (summer)
4 -- A-72 (summer)
5 -- A-72 (winter)
6 -- A-66 (summer)
7 -- A-66 (winter)
8 -- Temperature

Gasoline	ρ_4^{20}	γ, cst
A-66 summer	0.7193	0.5993
A-66 winter	0.6987	0.5343
A-72 summer	0.7332	0.6013
A-72 winter	0.7258	0.5423
A-76 summer	0.7840	0.5609
AI-93 summer (without TEL)	0.7550	0.6204
AI-93 summer (containing TEL)	0.7552	0.5254
Catalytic reforming		
ordinary regime	0.7305	0.5105
drastic regime	0.8114	0.6857
Catalytic cracking	0.7848	0.7127
Thermal cracking	0.7345	0.6895
Coking	0.7577	0.8152

[cst = centistokes]

An increase in viscosity is observed for individual monotypical-structure hydrocarbons, with increase in their molecular weight or in their boiling points. In paraffinic hydrocarbons with strongly branched chains, the viscosity is higher than in straight-chain hydrocarbons. The viscosity of naphthenic hydrocarbons rises rapidly with increase in the number of side chains and in their length.

The viscosity of hydrocarbons of different classes that are part of gasoline increases in the following order: normal-structure paraffinic, aromatic, and naphthenic [14].

The viscosity of automotive gasolines varies appreciably with change in temperature. The temperature coefficient of fuel viscosity increases with decrease in temperature and with increase in absolute viscosity values. In each homologous hydrocarbon series, the temperature coefficient increases with molecular weight. Naphthenic hydrocarbons, compared with aliphatic, exhibit a higher temperature coefficient of viscosity [14].

Fig. 9 presents the results of the determination of the kinematic viscosities of commercial automotive gasolines at various temperatures. All the experimental data are closely described by the Walter equation

$$\lg \lg (\nu + 0{,}8) = A - B \lg (t + 273{,}2)$$

where ν is the viscosity at temperature t, cst; A and B are constants determined by two experimental viscosity values taken at different temperatures.

With decrease in temperature, along with an increase in the viscosity of gasolines, the specific gravity increases. The specific gravity of automotive gasolines is determined by chemical composition and at ordinary temperatures (+20° C) varies within the range 0.690 to 0.810 g/cm^3.

Fig. 10 shows the experimental data from a determination of the specific gravities of automotive gasolines at various temperatures. Knowing the specific gravity of gasoline at 20° C, one can find its specific gravity at another temperature by using the formula

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

where β is the temperature correction, whose value depends on the specific gravity of gasoline:

ρ_4^{20}	β	ρ_4^{20}	β
0,6900—0,6999	0,000910	0,7600—0,7699	0,000818
0,7000—0,7099	0,000897	0,7700—0,7799	0,000805
0,7100—0,7199	0,000884	0,7800—0,7899	0,0007[illegible]
0,7200—0,7299	0,000870	0,7900—0,7999	0,0007[illegible]
0,7300—0,7399	0,000857	0,8000—0,8099	0,000765
0,7400—0,7499	0,000844	0,8100—0,8199	0,000752
0,7500—0,7599	0,000831		

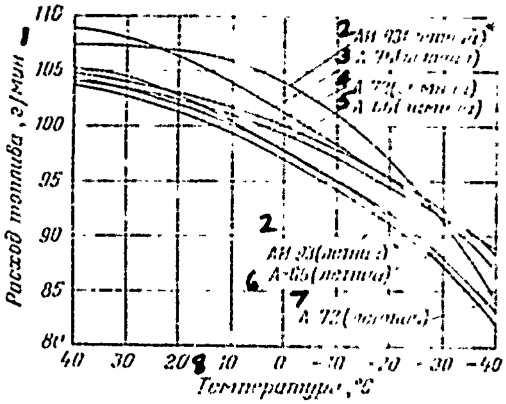

Fig. 11. Temperature dependence of volume flow of gasoline through jet nozzle. The gasolines were produced at different refineries.

Key: 1 -- Volume flow of fuel, g/min
2 -- AI-93 (summer)*
3 -- A-76 (summer)
4 -- A-72 (winter)
5 -- A-76 (winter)
6 -- A-66 (summer)
7 -- A-72 (summer)
8 -- Temperature

Also dependent on the specific gravity of gasoline is the fuel level in the carburetor chamber. The lower the specific gravity of a gasoline, the deeper the float is immersed in it and the higher will be the chamber level. In normal operation of an automotive engine, the gasoline level in the float chamber is set 3-5 mm below the upper cutoff of the spray nozzle. If the specific gravity of a gasoline is considerably less than the calculated value, the fuel level in the float chamber can increase to the extent that the gasoline will spontaneously float out of the spray nozzle.

The amount of fuel streaming through the carburetor jet nozzle depends on the viscosity and specific gravity of a gasoline. The higher the gasoline's specific gravity, the more of it will flow through the jet nozzles per unit time. The greater the viscosity of the fuel, the lower its flowrate through the jet nozzles, that is, the smaller its volume flow.

Thus, with a decrease in fuel temperature, its volume flow, on the one hand, increases (due to an increase in specific gravity), while on the other hand it decreases (due to an increase in viscosity).

To determine the overall effect of the various factors on fuel volume flow as a function of temperature, the flow of several gasolines through the main nozzle of a carburetor installed on a ZIL-130 engine was calculated. Experimental data on the viscosity and specific gravity of domestic gasolines determined in the range 40 to -40° C were used in the calculation.

The results (Fig. 11) show that with decrease in temperature there is a decrease in the volume flow of gasoline through the jet nozzle, that is, the change in viscosity plays a greater role in the overall effect than viscosity change.

The flow of gasoline through the jet nozzle when the temperature is varied from 40 to -40° C decreases by 20-30 percent. If here we take into account the changes in the physicochemical parameters of the air with temperature decrease, we can anticipate a considerable increase in the excess air coefficient. Approximate calculations showed that when the temperature is varied from 40 to -40° C on otherwise equal conditions, the excess air coefficient is increased by 30-40 percent.

Change in gasoline properties in various temperature conditions of vehicular operation dictates the necessity of seasonal norms for gasoline flow in automotive transportation.

Combustion of Mixtures of Gasoline Vapor With Air (Air-Gasoline Mixture)

By the term "combustion" as applied to automotive engines, we mean the rapid reaction of hydrocarbons and impurities in fuel with air oxygen, accompanied by incandescence and the evolution of a considerable amount of heat.

Combustion is the most important process responsible for the useful work done by an engine, since here the chemical energy of fuel is transformed into thermal energy, and further into mechanical energy. The combustion process determines the power-output and operating-economy indicators of an engine, and the nature of the process strongly affects engine reliability and service life [16].

In the question of fuel, heat is given off, whose amount depends on the composition of the combustible mixture and on the properties of the fuel itself. The ability of fuel to release a given amount of heat in complete combustion is dictated by its heat of combustion (heating value or heating ability). The heat of combustion can be related per kg (gravimetric) or per liter (volumetric) of fuel. A difference is made between the upper and lower heats of combustion. When determining the upper heat of combustion, we take into account the total of heat, including the heat evolved in the condensation of water formed in the combustion of hydrogen that is part of the composition of fuel hydrocarbons. The low heat of combustion does not take into account heat released in the condensation of water.

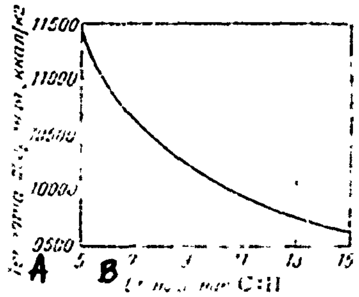

Fig. 12. Relationship between upper heat of combustion of gasolines and C:H ratio
Key: A — Heat of combustion, kcal/kg
B — C:H ratio

In internal combustion engines the temperature of the exhaust gas is higher than the temperature of condensation of water vapor, therefore in calculations the lower heat of combustion value is used. The value of the upper heat of combustion for gasolines is usually approximately 600 kcal/kg greater than the lower heat value.

The heat of combustion of fuel can be determined experimentally in calorimeters of various design or can be calculated roughly based on data on the elemental composition of fuel.

In the complete combustion of 1 kg of carbon to carbon dioxide, 8140 kcal of heat are given off, and in the complete combustion of 1 kg of hydrogen into water vapor — 28,000 kcal evolved.

The combustion of carbon and hydrogen combined in various compounds (hydrocarbons) proceeds much more complexly than for free carbon and hydrogen. The presence, for example, of a triple bond in hydrocarbons (acetylene) significantly increases the heat of combustion.

For practical purposes, the heat of combustion of fuel is determined by empirical formulas, for example, by formulas proposed by D. I. Mendeleyev:

$$Q_h = 81C + 300H - 26(O - S)$$
$$Q_l = 81C + 246H - 26(O - S)$$

where Q_h is the higher heat of combustion of fuel, kcal/kg; Q_l is the lower heat of combustion, kcal/kg; C, H, O, and S of the fuel content of carbon, hydrogen, oxygen, and sulfur, respectively, percent.

Satisfactory results are also provided by an empirical formula

$$Q_1 \approx 705\ L_0$$

where L_0 is the theoretically needed amount of air, kg/kg of fuel.

To calculate the lower heat of combustion (in kcal/kg) based on the known value of the upper heat of combustion of fuel, we can use the following formulas:

$$Q_1 = 0.75\ Q_h + 2000$$

$$Q_1 = Q_h - (4400 \cdot H/C).$$

A relationship between the heat of combustion and the carbon/hydrogen ratio exists for hydrocarbons. The largest ratio for a hydrocarbon, the lower is its gravimetric heat of combustion (Fig. 12).

Paraffinic hydrocarbons have the highest gravimetric heat of combustion. The heat of combustion decreases with increase in molecular weight. Aromatic hydrocarbons have the lowest gravimetric heat of combustion, increasing with their molecular weight (Table 9).

Therefore gasolines containing predominantly paraffinic hydrocarbons will be characterized by a higher gravimetric heat of combustion than gasolines containing considerable amounts of aromatic hydrocarbons (catalytic cracking gasolines and especially, drastic-regime catalytic reforming gasolines).

The isomeric structure of hydrocarbons does not strongly affect their heat of combustion (cf. Table 9).

The carbon/hydrogen ratio to some extent determines the specific gravity of a hydrocarbon: with increase in the ratio for a hydrocarbon, its specific gravity becomes greater. On this basis, Ye. Bass suggested a formula for calculating the lower heat of combustion (in kcal/kg) of a hydrocarbon fuel based on its specific gravity:

$$Q_{sat} = (22320 - 3780\rho_4^{15})\ 0,5:$$

It must be noted that the Ye. Bass formula for gasolines provides quite satisfactory results.

The data given in Table 9 indicate that hydrocarbons and hydrocarbon fuels only differ slightly in their heats of combustion, therefore an increase in engine power output or operating economy through these gasolines with a higher "energy reserve" does not appear possible. No additives

Table 9. Heat of combustion of certain hydrocarbons and fuels

Углеводород и топливо 1	ρ_4^{20}	L_0, кг/кг 2	Низшая теплота сгорания 3	
			ккал/кг 4	ккал/л 5
Бутан 6	0,579	15,48	10 931	6328
Пентан 7	0,626	15,35	10 841	6786
2-Метилбутан 8	0,620	15,35	10 832	6716
Октан 9	0,703	15,15	10 670	7501
Изооктан 10	0,692	15,15	10 656	7374
Пентен-1 11	0,610	14,80	10 757	6874
Октен-1 12	0,7144	14,80	10 650	7608
Циклопентан 13	0,745	14,80	10 567	7872
Циклогексан 14	0,779	14,80	10 480	8164
Бензол 15	0,879	13,28	9 763	8582
Толуол 16	0,867	13,51	9 789	8487
Пропилбензол 17	0,863	13,80	9 943	8581
Метиловый спирт 18	0,791	6,5	4 600	3639
Этиловый спирт 19	0,795	9,0	6 300	5008
Бензины 20				
прямой перегонки 21	0,724	~15,1	10 600	7674
термического крекинга 22	0,7345	~14,9	10 550	7717
каталитического крекинга 23	0,7818	~14,6	10 420	7721
каталитического риформинга 24	0,7305	~14,3	10 260	7921
Б-70 25	0,738	~15,0	10 400	7675
А-76 зимний 26	0,6987	~15,0	10 620	7593
А-76 летний 27	0,7300	~15,0	10 500	7665
АИ-93 летний 28	0,7552	~14,5	10 310	7867
Керосин 29	0,822	~15,0	10 300	8466

Key:

1 -- Hydrocarbon and fuel	16 -- Toluene
2 -- kg/kg	17 -- Propylbenzene
3 -- Lower heat of combustion	18 -- Methyl alcohol
4 -- cal/kg	19 -- Ethyl alcohol
5 -- kcal/l	20 -- Gasolines
6 -- Butane	21 -- Straight-run
7 -- Pentane	22 -- Thermal cracking
8 -- 2-Methylbutane	23 -- Catalytic cracking
9 -- Octane	24 -- Catalytic reforming
10 -- Isooctane	25 -- B-70
11 -- Pentene-1	26 -- A-76, winter
12 -- Octene-1	27 -- A-76, summer
13 -- Cyclopentane	28 -- AI-93, summer
14 -- Cyclohexane	29 -- Kerosene
15 -- Benzene	

have yet been found that sharply increase the heat of combustion. For special purposes, the heat of combustion of hydrocarbon fuels is increased by using individual acetylene hydrocarbons, by adding metallic suspensions, boron hydrides, and so on. However, these methods are quite expensive and are limited in resources, therefore can be scarcely applicable to such mass-produced fuels as automotive gasolines.

A mixture of fuel and air burns in engines, therefore for the energy evaluation of fuel not only is its heat of combustion important, but also the amount of heat released in the combustion of an air-fuel mixture with stoichiometric composition (with $\alpha = 1$). Its value depends on the heat of combustion of the fuel and the amount of air in such mixture.

The amount of air required for combustion is increased for hydrocarbons with increased heats of combustion. Accordingly, the amount of heat released in the combustion of various air-fuel mixtures changes very slightly:

	L_0, kg/kg	Q, kcal/m^3
Automotive gasoline	15.0	824
Aviation gasoline	15.0	826
Benzene	13.3	820
Ethyl alcohol	9.0	825

The heat of combustion of the air-alcohol mixture bears noting. Alcohols contain a large amount of oxygen and the heat of combustion is moderate. But the presence of oxygen in alcohols also reduces the amount of air required for combustion, therefore in the combustion of an air-alcohol mixture practically speaking just as much heat is released as in the combustion of the same volume of an air-gasoline mixture.

In the complete combustion of an air mixture of automotive gasolines having various compositions, 820-830 kcal/m^3 of the mixture, or 665-675 kcal/kg is released. However, in practice considerably less heat is released in the engine since the composition of the mixture is inhomogeneous and in various parts of the combustion chamber the fuel does not achieve a stoichiometric ratio with air. The heat of combustion of a mixture admitted into an engine also depends on the overall excess air coefficient.

To calculate the combustion of the mixture in which the air excess coefficient and the completeness of combustion are not equal to unity, one can use the following formula:

$$H_1 = Q_1\eta/(1 + \alpha L_0) ,$$

where H_1 is lower heat of combustion of the combustible mixture, kcal/kg and η is the coefficient of fuel combustion completeness.

The combustion of air-gasoline mixtures in engines is an extremely complicated chemical process, developing in conditions of rapidly changing temperatures, pressures, and reagent concentrations. The combustion reactions ordinarily occur as several successive stages and as several parallel competing processes. A study of chemical transformations in the combustion of a mixture of hydrocarbons that is as complicated as gasoline involves major difficulties. The diversity of the reactions can be demonstrated with the example of the simplest hydrocarbons -- methane. Academician N. N. Semenov maintains that the high-temperature oxidation of methane proceeds according to the following radical-chain scheme [17]:

$$\begin{gathered}
CH_4 + O_2 \rightleftarrows \dot{C}H_3 + HOO\cdot \\
\dot{C}H_3 + O_2 \rightleftarrows HCHO + \dot{O}H \\
\dot{O}H + CH_4 \rightleftarrows \dot{C}H_3 + H_2O \\
\dot{O}H + HCHO \rightleftarrows H\dot{C}O + H_2O \\
HCHO + O_2 \rightleftarrows H\dot{C}O + HOO\cdot \\
H\dot{C}O + O_2 \rightleftarrows CO + HOO\cdot \\
CH_4 + HO\dot{O} \rightleftarrows H_2O_2 + \dot{C}H_3 \\
HCHO + HO\dot{O} \rightleftarrows H_2O_2 + H\dot{C}O
\end{gathered}$$

The beginning of the chain is the active collision of methane and oxygen molecules, resulting in two radicals being formed: $\dot{C}H_3$ and $H\dot{O}_2$. In subsequent stages, radicals like $\dot{O}H$ and $H\dot{C}O$ participate, along with the relatively stable intermediate products -- formaldehyde and hydrogen peroxide.

The carbon monoxide formed during the reactions can burn according to the following scheme [18]:

$$\begin{gathered}
CO + \dot{O}H \rightleftarrows CO_2 + \dot{H} \\
\dot{H} + O_2 \rightleftarrows \dot{O}H + O \\
CO + O \rightleftarrows CO_2
\end{gathered}$$

Thus, even in the combustion of the simplest hydrocarbon -- methane -- a whole complex of various elementary acts occurs, whose rate is responsible for the composition of the products formed at each given instant and for the overall rate of the process as a whole. A wealth of experimental material enables us to regard the above-presented mechanism for methane oxidation as established, although there are areas that are still unclear.

The high-temperature oxidation of more complicated hydrocarbons of various structures has been studied very little owing to the even more complicated pattern of the processes that occur.

One must delimit two processes in the combustion of hydrocarbon fuels -- the process of ignition (initiation of combustion) and the process of flame propagation.

To ignite a flammable mixture, energy must be brought from without in amounts sufficient to ensure in some volume of the mixture the initial rates of chemical reactions at which heat release begins to exceed the rate of heat removal from the reacting mixture toward the walls or into the ambient colder regions of the mixture [18]. Ignition of a mixture can occur through self-ignition or by forced ignition. Self-ignition of a flammable mixture occurs in conditions when self-accelerating chemical processes begin to develop throughout the volume of the mixture or in some regions of it of relatively small volume, cumulating in the initiation of flame. Self-ignition can proceed via the heating of the combustible mixture from the vessel walls, by adiabatic or shock compression, and so on.

Ignition is intense local heat from an outside source of a small region of a combustible mixture to high temperatures. Usually, the ignition process is accomplished with an electrical spark; and the mixture in the discharge zone is heated virtually instantaneously to a temperature somewhat exceeding its combustion point. The rates of chemical reactions in the spark discharge zone reach enormous values. After cessation of the discharge, the reaction rates fall to values corresponding to the combustion conditions of the given mixture in the flame front.

The ignition of air-hydrocarbon mixtures, owing to the complex chain mechanism of preflame processes, can be of the one- or multi-stage type, depending on the temperature and pressure of the medium and the construction of the hydrocarbons constituting the mixture. In some conditions, ordinary ignition (heated explosion) of a mixture can be proceeded by the appearance of a so-called cold flame -- a special intermediate stage of the oxidative process accompanied by relatively small rise in temperature (about 100° C) and with a weak blue-violet glow, discernible only in darkness. It is believed that the cause of the glow is the chemoluminescence caused by excited formaldehyde molecules. Cold-flame self-heating of a combustible mixture was made clearly evident in bomb investigations as a characteristic jump on indicator diagrams [18].

In contrast to ignition, the flame propagation process proceeds spontaneously, without any effect on the combustible mixture. Successive layers or volumes of the combustible mixture ignite due to energy released in the combustion of the preceding portions of the same mixture.

Flame propagation processes are differentiated by the methods of energy transport from the heated layers into the fresh mixture. A distinction is made between diffusion-chain and thermal propagation of flame [18]. Diffusion from the combustion zone into the fresh mixture of active centers causing chain reactions in new layers plays a basic role in the diffusion-chain mechanism of flame propagation, while in thermal propagation processes of heat transport from the combustion zone into the fresh mixture are fundamental. When flame propagates in the combustion chamber of an engine, two mechanisms are at work, but the significance of each changes with progression of the combustion process. Immediately after ignition of a combustible mixture, the main role in the propagation of flame belongs to the diffusion-chain processes, while later thermal processes take on predominant importance.

The flame propagation rate depends also on the condition of the mixture before ignition. If the mixture is still or is flowing laminarly, transport processes in the flame front proceed via molecular diffusion and thermal conductivity. This kind of flame propagation is called laminar. If the combustible mixture is in turbulent motion, molecular diffusion begins to play a secondary role -- processes of turbulent mixing of the fresh mixture with combustion products take on principal importance in flame propagation [18]. This kind of combustion is called turbulent.

In a study of combustion processes in bombs and pipes at low mixture flowrates, laminar flame propagation occurs and the combustion rate is 1-4 m/sec.

Internal combustion engines are filled with the working mixture at high rates: a strong eddy motion is produced, which partially persists even during the compression period. In these conditions, combustion is turbulent and the flame propagation rate rises markedly -- to 10-40 m/sec.

An increase in the velocity of flame front propagation with greater turbulence of the combustible mixture occurs also due to curving and enlargement of the flame front surface and is very significant in ensuring normal combustion of a mixture in an engine at different rpms. With increase in rpm, the time provided for the combustion process in the chamber decreases steadily. At the same time the eddy motion of the mixture intensifies through an increase in the rate at which the mixture is admitted through the intake valve, leading to a rise in the flame propagation velocity. The effect of the turbulence in the working mixture on the velocity of flame front propagation [19] shown below:

Flowrate of mixture through intake valve, m/sec	Intensity of eddy motion of mixture in engine cylinder, m/sec	Velocity of flame front propagation, m/sec
6	1	6
12	2	10
18	3	14
24	4	18
30	5	21
31	6	22

Thus, the velocity of flame front propagation increases roughly in proportion to the crankshaft rpm (Fig. 13). But if the velocity of flame front propagation did not depend on mixture turbulence, operation of the engine in various regimes would be impossible.

The velocity of flame front propagation increases with a rise in pressure and temperature. Accordingly, a higher compression ratio,

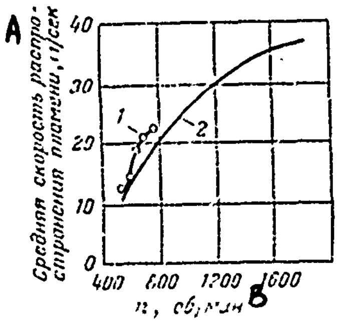

Fig. 13. Effect of crank rpm on mean flame propagation rate [20, 21]:
1 -- based on Chudakov's data
2 -- based on Taylor's data
Key: A -- Mean rate of flame propagation, m/sec
B -- rpm

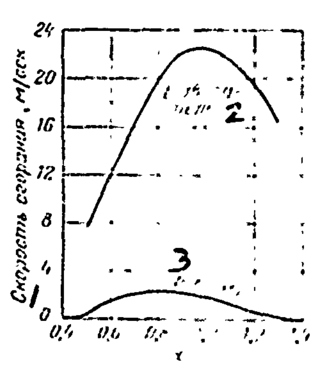

Fig. 14. Effect of composition of air-gasoline mixture on its combustion rate in engine and in bomb
Key: 1 -- Combustion rate, m/sec
2 -- In engine
3 -- In bomb

supercharging, and other measures raising pressure and temperature at the end of the compression stroke lead to a rise in the velocity of flame front propagation.

The velocity of flame front propagation depends on the mixture composition, that is, on the air excess coefficient. The maximum velocity corresponds to $\alpha = 0.90$ (Fig. 14). When a mixture undergoes enrichment or leaning, the velocity of flame front propagation becomes less. In the first case, this occurs owing to an oxygen deficiency, and in the second case -- owing to the expenditure of some of the heat in the heating the excess air. It must noted that the maximum in the flame velocity cannot coincide with respect to α when tests are made in engines and in a bomb (Fig. 14).

For some values of the coefficient α, an excess of air or fuel is produced in the mixture so that most of the energy from the ignition source is dissipated and expended in heating excess amounts of air or fuel, and the velocity of flame front propagation in these cases drops to zero. These values of α taken as the limits of flame propagation. As a rule, the limits of flame propagation are at the same time the limits of mixture ignitability, since beyond these limits a local ignition source is incapable of ensuring the propagation of the combustion process throughout the volume of the mixture.

Table 10 gives the concentration limits to the propagation of a laminar flame for several individual hydrocarbons and alcohols. For most hydrocarbon motor fuels, the concentration limits to the propagation of a laminar flame at atmospheric pressure and 20° C are as follows: upper -- 0.25-0.37; and lower -- 1.65-1.80. Alcohols exhibit a somewhat greater limit of possible leaning. The limits shown in the table relate to the propagation of a laminar flame in large-diameter pipes (>50 mm), when the relative heat losses in the walls owing to thermal conductivity are low.

It must be noted that the ignitability limits of air-fuel mixtures in an engine depend not only and not so much on chemical composition of fuel, as on the conditions of ignition and combustion. Here we refer first of all to the intensity of ignition, the temperature of the mixture at the instant of ignition, mixture turbulence, and so on.

For the conditions of ignition and turbulence occurring in an engine (but at standard conditions: temperature 20 ° C and pressure 760 mm Hg), the limits to the ignitability of certain fuels and hydrocarbons are presented in Table 11.

The limits to ignitability listed are significantly narrower than those presented earlier for the propagation of laminar flame in pipes.

Earlier it was noted that with a rise in temperature and pressure, the limits to the ignitability of mixtures are enlarged, Accordingly, it is customarily to assume that in an engine the α values are the same: approximately 0.4-0.5 for the upper limit to the ignition of an air-gasoline mixture, and 1.3-1.4 -- for the lower limit. These limits are valid for the conditions in which an ordinary single-head spark plug ignites. Academician Ye. A. Chudakov succeeded in achieving the reliable ignition of an air-gasoline mixture in which the excess air coefficient was 1.5-2.0 [21]. Igniting a mixture with this composition was attained by using a multi-head or by prior heating of the mixture in the ignition zone.

The question of expanding the limits to the stable combustion of a working mixture, in particular increasing the combustion rate, of specially lean mixtures and ensuring their reliable ignition is vitally practical, since its solution can raise the operating economy of a gasoline. When an engine is run on lean mixtures, higher indicator efficiencies are achieved through a reduction in the temperature of combustion products and in their dissociation, a decrease in heat removal in walls, and so on. Overall, this leads to a substantial fuel savings in partial loads [18].

An especially simple solution to the problem of significantly extending the limits to the effective use of lean mixtures in gasoline engines on partial loads, with the simultaneous preservation of high power-output operating-economy indicators at full loads, is afforded by the prechamber-burner ignition scheme developed by A. S. Sokolik, A. N. Voinov, and L. A. G.ssak [18].

Table 10. Concentration limits of flame propagation (at 760 mm Hg and 15-20° C) [14]

Топливо 1	Верхний предел 2		Нижний предел 4	
	объемн. % 3	α	объемн. % 3	α
н-Бутан 5	8,5	0,35	1,9	1,66
Бутилен 6	9,6	0,33	2,0	1,71
н-Гексан 7	7,4	0,27	1,2	1,81
Циклогексан 8	7,7	0,28	1,3	1,77
Бензол 9	7,1	0,37	1,4	1,96
Толуол 10	6,7	0,32	1,3	1,77
Изооктан 11	6,0	0,26	1,0	1,65
о-Ксилол 12	6,0	0,31	1,0	1,97
Метиловый спирт 13	36,0	0,25	6,7	1,95
Этиловый спирт 14	19,0	0,30	3,3	2,03
Бутиловый спирт 15	11,2	0,28	1,4	2,46

Key: 1 -- Fuel
2 -- Upper limit
3 -- percent by volume
4 -- Lower limit
5 -- n-Butane
6 -- Butylene
7 -- n-Hexane
8 -- Cyclohexane
9 -- Benzene
10 -- Toluene
11 -- Isooctane
12 -- o-Xylene
13 -- Methyl alcohol
14 -- Ethyl alcohol
15 -- Butyl alcohol

Table 11. Combustibility limits of air-fuel mixtures (760 mm Hg, 20° C) [19]

Топливо 1	Верхний предел 2		Нижний предел 4	
	объемн. % 3	α	объемн. % 5	α
Автобензин 6	2,58	0,609	1,67	1,10
Авиабензин 7	3,04	0,675	1,83	1,13
Бензол 8	2,81	0,725	2,00	1,14
Изооктан 9	2,30	0,718	1,61	1,03

Key: 1 -- Fuel
2 -- Upper limit
3 -- percent by volume
4 -- Lower limit
5 -- percent by volume
6 -- Automotive gasoline
7 -- Aviation gasoline
8 -- Benzene
9 -- Isooctane

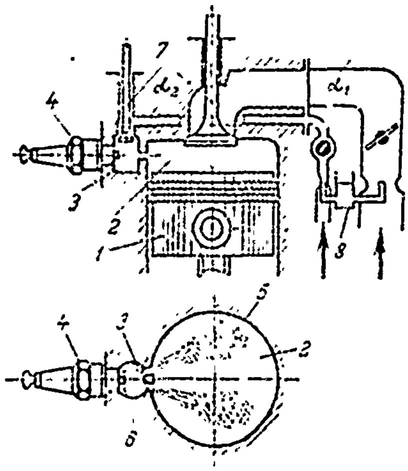

Fig. 15. Schematic diagram of carburetor engine with prechamber burner ignition [22]:

1 -- piston
2 -- main combustion chamber
3 -- prechamber
4 -- spark plug
5 -- flame gas burner
6 -- nozzle openings
7 -- intake valves (main and auxiliary)
8 -- two-section carburetor
α = lean mixture
α_2 = rich mixture

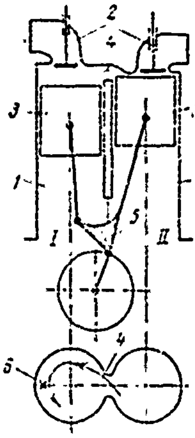

Fig. 16. Engine designed by V. M. Kushul'

1 -- paired cylinders I and II
2 -- intake valves
3 -- pistons
4 -- tangential channel
5 -- pin of knuckle connecting rod
6 -- spark plug

The principle of prechamber-burner ignition involves igniting the working mixture in a cylinder not with a spark plug, but with the tip of a flame formed in the combustion of a small amount of enriched mixture in a special prechamber connected to the main combustion chamber by several channels. The prechamber volume is only 2-3 percent of the volume of the main combustion chamber. A spark plug and a small auxiliary intake valve opening at the same time as the main intake valve by means of a common drive are located in the prechamber (Fig. 15). Enriched mixture ensuring the most favorable conditions for ignition and the propagation of the initial combustion locus is fed through the auxiliary intake system into the prechamber. After ignition of the mixture in the prechamber, the pressure rises rapidly and gases continuing to burn are ejected through the openings into the main chamber, where after a very short delay the lean mixture ignites practically simultaneously at a large number of points along the flame periphery. This strong ignition of a mixture that has been additionally made turbulent by the flame leads to intensely leaned mixtures with an excess air coefficient $\alpha = 1.7$-1.8 being made capable of burning in the cylinder at high enough rates [18].

Prechamber-burner ignition at the present time has found practical use in several modifications of domestic and foreign engines [23, 24].

Leaning a mixture to regulate power output is provided for an engine of original design developed by V. M. Kushul' [25]. His engine has twin cylinders placed side by side, connected with each other into the head cavity (Fig. 16). Piston travel occurs with a phase shift: the piston of cylinder II lags somewhat behind the piston of cylinder I (22-30° of a full crank revolution). Cylinder I is filled with an enriched air-gasoline mixture, and cylinder II -- with pure air.

Cylinder I has a combustion chamber whose volume corresponds to a compression ratio of about 6.5. Cylinder II has no combustion chamber and as its piston approaches TDC the entire air charge is displaced into the combustion chamber of cylinder I. The total compression ratio with respect to both cylinders and thus the expansion ratio corresponds to approximately 11.

The mixture in cylinder I is ignited with a spark at 10-12° before the piston reaches the TDC. The compression pressure at this instant is about the same in both cylinders. Air is blown from cylinder II during the combustion of the mixture in cylinder I; the air causes intense turbulence and vigorous final ignition of the mixture in cylinder I.

Adjustment of the load in the V. M. Kushul' engine in the range from maximum to half load is achieved by leaning the mixture arriving in cylinder I with $\alpha = 0.5$ to $\alpha = 1.0$, corresponding to a change in α, with respect to both cylinders, from 1.0 to 2.0.

In 1959 a new process with stratified charge distribution in the combustion chamber was patented in the United States [1]. According to the patent description, an eddy air stream along the cylinder walls produced during intake and continuing during compression, and the injection of fuel through a nozzle located in the combustion chamber directly into this eddy produces a zone of enriched mixture in the chamber center -- in the spark plug zone. The intense combustion beginning here spreads to the periphery, as a result which mixtures with α values to 3.5 burned. The proposed process has been considerably improved at the present time and is used in several series-manufactured automotive engines in the United States [2-5].

At the VII World Petroleum Congress in Mexico [26], French Institute of Petroleum proposed a unique method of carburetion and ignition of air-fuel mixtures. An air-fuel mixture is fed via two ducts. A rich mixture is supplied through one channel, and it is directed toward the spark plug; and a lean mixture or pure air is supplied through the other. The duct for the rich mixture is a thin tube placed within the duct for the lean mixture. The rich mixture can be fed through the hollow stem of the exhaust valve. The fuel mixture fed into the cylinder is not homogeneous, which promotes the more rational beginning of the combustion process. The inventors showed that this combustion reduces the carbon monoxide and unburned hydrocarbon content in exhaust gases [26].

In the normal working process in spark ignition engines, mixture combustion can be provisionally subdivided into three phases: the first is the initial phase during which a small combustion locus induced between the spark plug electrodes is gradually converted into a well-developed front of turbulent flame. The second is the main flame propagation phase; and the third is the phase of final mixture combustion. It is not possible to draw a sharp boundary between the individual combustion phases since the change in the nature of the process occurs gradually.

The first phase begins from the instant a spark jumps between the spark plug electrodes. Initially the combustion locus is very small; the flame velocity is low; and it is close to the velocity of laminar combustion. Excess turbulence of the mixture in the spark plug zone leads to intensified heat removal from the combustion zone and makes the progression of the flame locus unstable [22]. Therefore the spark plug is usually placed in a small recess in the combustion chamber wall. In the initial period the combustion rate is determined by the physicochemical properties of the combustible mixture and depends relatively little on the intensity of turbulence [22].

The duration of the initial phase is customarily measured by the time interval from the moment the spark appears (point a in Fig. 17) to the "separation point" of the combustion line from the compression line on the indicator diagram (point b in Fig. 17), that is, to the instant when a perceptible pressure rise as a result of combustion commences [22]. On analogy with diesel engines, this interval is sometimes called the combustion delay period over the induction period, which is incorrect in principle [18]. In spark ignition, combustion delay is virtually absent; a flame locus appears at once about the spark plug electrodes, but there is a period during which the flame front spreads relatively slowly from this locus and the fraction of the burning mixture is still so small that no pressure rise can be detected in the indicator diagram.

The second phase of the combustion process, whose onset is taken as the "separation point" of the combustion line from the compression line (cf. Fig. 17), is characterized by a sharp rise in the combustion rate owing to intense turbulence of the mixture. During this phase the combustion rate is determined by the intensity of mixture turbulence and depends little on the physicochemical properties of the mixture. The turbulence of the mixture, as indicated above, rises in proportion to the crankshaft rpm, therefore the duration of the main combustion phase expressed in

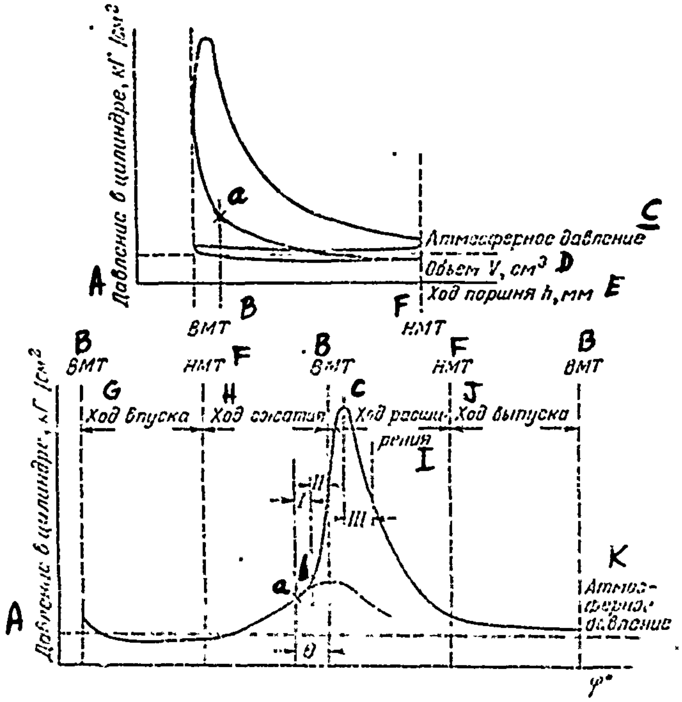

Fig. 17. Rotated (along piston stroke) and evolved (along crank angle) indicator diagrams [16]:

θ = ignition advance angle
a = instant of spark plug ignition feed
b = instant of beginning of flame front propagation
c = instant of attaining maximum pressure in combustion chamber
I -- period of latent combustion
II -- period of propagation of flame front
III -- period of final combustion of mixture

Key: A -- Pressure in cylinder, kg/cm²
B -- TDC [top dead center]
C -- Atmospheric pressure
D -- Volume, V, cm³
E -- Piston travel, h, mm
F -- BDC [bottom dead center]
G -- Intake stroke
H -- Compression stroke
I -- Work stroke
J -- Exhaust stroke
K -- Atmospheric pressure

degrees of crank angle virtually independent of the engine velocity regime. Measurements show that over some sections in the combustion chamber the flame propagation velocity is 50-60 m/sec at high rpms.

It is customary to take as the boundary between the main and the culminating combustion phases the instant at which the pressure maximum is reached in the indicator diagram (point c in Fig. 17). Combustion during this time has not yet been completed and the mean temperature of the gases in the cylinder continues to rise for some time [22]. The flame front by now approaches the combustion chamber walls and its propagation rate decreases owing to the lower intensity of turbulence and the temperature drop in the layers adjoining the walls. The drop in the combustion rate leads to a lower heat release rate, therefore the pressure rise resulting from combustion in the phase of final combustion no longer can compensate for its decrease owing to the beginning working stroke of the piston. The processes of final mixture combustion in the layers adjoining the combustion chamber walls continue for a fairly long time. Here the rate of the final combustion, just as the combustion rate in the initial phase depends more on the physicochemical properties of the working mixture than on the intensity of its turbulent motion [22].

It must noted that the efficiency of the working process in an engine cylinder, and thus the maximum power and operating economy of an engine under otherwise equal conditions are determined by the duration and "timing" of the combustion of a working mixture.

The higher the combustion rate, the more power an engine will develop for the same fuel expenditure. This occurs because as the combustion rate is increased, the working cycle of the engine approaches the theoretical value in which instantaneous combustion of the entire charge at the TDC is assumed. The closer the fuel to the TDC, the more complete will be the subsequent expansion of the combustion products and thus the less heat will be carried off with the gases. However, when the combustion process occurs very rapidly, major shock loads occur at the crank-connecting rod mechanism parts, characterized by the "rough" operation of the engine [16].

In modern high-speed carburetor engines with a compression ratio of 7-8, the length of the main combustion phase is 25-30° crank angle, which corresponds to 0.0025 sec at 2000 rpm. With this duration of the main combustion phase, the "roughness" of engine operation, rated by the pressure rise rate in the combustion chamber with respect to the crank angle [22] is 1-1.2 (kg/cm^2·deg) -- for engines having a compression ratio of 6-7, and it is 1.5-2.0 (kg/cm^2·deg) -- for engines with a compression ratio of 8-10.

The "timing" of combustion process is significantly regulated by the instant the mixture is ignited with a spark, that is, the ignition advance angle. If the mixture is ignited too late, shown in Fig. 18 a, combustion can begin during the power stroke, and in this case the engine power will fall and its operating economy will deteriorate. If the mixture is ignited too early (Fig. 18 c), its combustion will occur mainly still during the time of the compression stroke, and in this event power losses in overcoming the pressure of gases at a piston as it moves toward the TDC will rise considerably (the hatched region in the diagram).

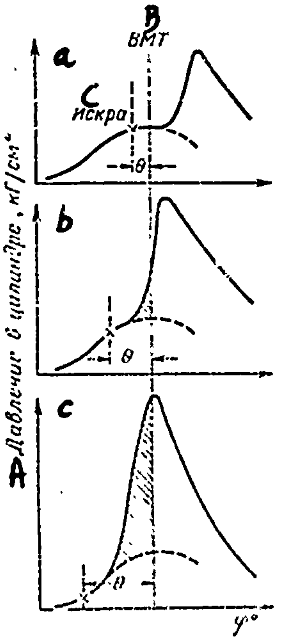

Fig. 18. Effect of ignition advance angle on the shape of the indicator diagram [16]:
a -- for late ignition
b -- for normal ignition
c -- for early ignition
Key: A -- Pressure in cylinder, kg/cm^2
B -- TDC
C -- Spark

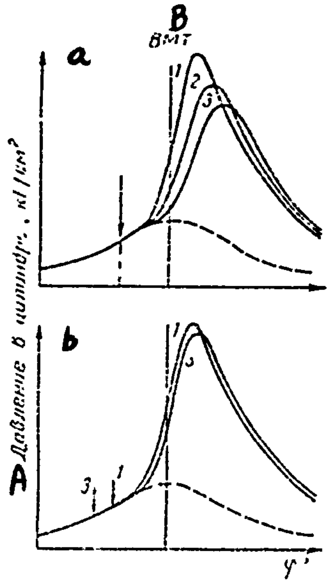

Fig. 19. Indicator diagrams of carburetor engine for different rpms:
a -- at constant ignition advance angle
b -- at optimal adjustment of instant of ignition
I -- n = 1000 rpm
II -- n = 2000 rpm
III -- n = 3000 rpm
Key: A -- Pressure in cylinder, kg/cm^2
B -- TDC

The most advantageous is the ignition advance for which the main combustion phase lies symmetrical to the TDC in the indicator diagram. Here the pressure rise as the result of combustion begins 12-15° BTDC, and the maximum pressure is attained over 12-15° crank turn passed the TDC.

However, the ignition advance cannot remain constant when there is a change in the crank rpm and in the engine load.

We have already noted that an increase in the crank rpm and the associated buildup of mixture turbulence have practically no effect on the duration of the first phase. Therefore, with ignition advance unchanged, as the rpm setting increases, increasingly later buildup of the combustion product in the cycle will be observed (Fig. 19 a).

When there is an appropriate increase in the ignition advance with rise in rpm setting, approximately constant arrangement of the main combustion phase can be achieved. Accordingly, a centrifugal governor of ignition advance is installed in modern engines; it varies the angle as a function of the crank rpm. A vacuum governor is installed in modern engines to regulate the ignition advance when there is variation in the engine load (degree of throttle opening).

It must be noted that the proper choice of the characteristics of the ignition advance governors significantly affects the engine requirements posed on the quality of the fuel used, but these requirements are associated with the phenomenon of knocking in the engine.

Knocking

In some automotive operating regimes usually associated with heavy loads, when gasoline is used whose quality does not fully measure up to the engine requirements, a special kind of combustion of the working mixture can occur, so-called detonation [knocking]. This combustion is accompanied by the appearance of a characteristic metallic rapping, and increase in exhaust smokiness, and a rise in the temperature in the engine cylinders.

All external signs and manifestations of knocking are well known, however the reasons for the occurrence and mechanism of this phenomenon has thus far not been fully clarified. There are several theories accounting for detonation knocking, but of these, the so-called peroxide theory is the most generally accepted at the present time.

Underlying this theory are the studies by the eminent Russian scientist, Academician A. N. Bakh, was established that in the oxidation of hydrocarbons, the primary products are the peroxide compounds of the type hydroperoxide R-O-O-H or dialkylperoxide R-O-O-R. The peroxides are classified as highly unstable compounds exhibiting high excess energy. At certain temperatures and pressures, peroxide compounds can break down spontaneously, giving off large amounts of heat and forming new active molecules.

The oxidation of gasoline hydrocarbons by air oxygen begins from the time gasoline is produced at a refinery and continues until gasoline is burned in an engine. The oxidation rate depends on temperature. With an increase of 10° C in the gasoline temperature, its oxidation rate rises about 2.2-2.4 times.

In the storage and transporting of gasoline, its temperature is usually low, therefore the oxidation of hydrocarbons and the formation of peroxide compounds proceeds extremely slowly. Peroxide compounds do not accumulate in these conditions, but undergo further oxidation, forming gummy substances.

The vigorous oxidation of gasoline hydrocarbons begins in the combustion chamber at the end of the working mixture compression stroke. As the piston travels to the TDC, temperature and pressure steadily rise in the working mixture and not only does the rate of oxidation of hydrocarbons increase, but also more and more of various kinds of compounds are involved in the oxidation process. Oxidation processes acquire especially high rates after ignition of the mixture and the formation of a flame front. With increasing combustion of the working mixture, temperature and pressure in the combustion chamber increase rapidly, which promotes further intensification of oxidation processes in the unburned portion of the working mixture. High temperatures and pressures act longest on the last portions of unburned fuel situated in front of the flame front. As a consequence, peroxide compounds accumulate especially intensely in these portions, and therefore the most favorable conditions for the conversion of normal combustion to detonation combustion are produced when precisely these latter portions of the working mixture are burned.

The above-described oxidation of hydrocarbons with formation of peroxide compounds occurs always in an engine, regardless of which combustion is present: normal or detonation [knocking].

If an engine uses a gasoline whose composition has a predominance of hydrocarbons that do not form -- upon oxidation -- large amounts of peroxide compounds, the concentration of peroxide in the last portions of the mixture does not reach critical values, and combustion concludes normally, without the initiation of detonation.

If during the oxidation of gasoline, many peroxide compounds accumulate in the last portions of the mixture, then above a certain critical value their explosive decomposition takes place, with the formation of so-called "cold flame." The combustion products in this flame are principally aldehydes and CO, so that the energy release in the "cold flame" represent only a small portion of the total heat of combustion of the fuel (5-10 percent), with a correspondingly temperature rise. The glow of a cold flame is due to the optical excitation of formaldehyde molecules immediately upon their formation, that is, it occurs owing to the energy of chemical reaction (chemiluminescence).

The spread of the cold flame through the working mixture, in contrast to normal hot flames, takes place exclusively by diffusion into the fresh mixture of active particles, which are radicals formed during the breakdown of the peroxides. A result of the cold-flame stage is the replacement of the initial, relatively inert hydrocarbon by a chemically active mixture of volcanic peroxides, aldehydes, and free radicals. This active mixture undergoes further oxidation and after some induction period, a new explosive decomposition of peroxide compounds occurs, similar to the preceding ne, but with the involvement of a greater mass of the initial mixture and with the participation of more of the peroxide compounds. A special type of flame develops, intermediate between cold and hot, which is called the "secondary cold flame" by A. S. Sokolik [27]. The reaction occurs just as in the cold flame, but not to the end products CO_2 and H_2O, but to CO, and the extent of heating in this flame is already large and corresponds to the evolution of roughly half of the total energy of combustion, therefore the "secondary cold flame" spreads at a greater rate not only owing to the diffusion of active centers, but also to heat transfer. After the passage of the "secondary cold flame," a mixture of CO and the unused oxygen remains to be heated to high temperatures. At a sufficiently high concentration of active centers, this mixture undergoes a chainwise-thermal explosion, producing a true hot flame, that is, self-ignition occurs [27].

Initially self-ignition and the formation of the new front of the hot flame occur at one or several places in the unburned portion of the working mixture. Simultaneous with the new hot flame front, the new front of a shock wave develops. Shock waves spreading through the heat of active mixture in which preflame reactions are close to completion, stimulate the self-ignition of the remaining unburned portion of the working mixture. And the rate of propagation of the hot flame front into the remaining portion of the mixture becomes the same as the velocity of shock wave propagation, that is, a detonation combustion wave having a velocity up to 2000-2500 m/sec appears.

Thus, essentially the phenomenon of detonation consists in the extremely rapid culmination of the combustion process resulted from multi-stage self-ignition of a portion of the working mixture in front of the flame front accompanied by the initiation of shock waves, which in turn stimulate the combustion of the entire remaining portion of the mixture at a supersonic velocity.

The above-presented concepts of the chain mechanism of detonation combustion are based on studies by Academician N. N. Semenov and have been confirmed by numerous experimental data.

Fig. 20 illustrates the studies made of the movement of the flame front in normal and detonation combustion of a mixture in a special engine equipped with a high-speed motion picture camera. The locus of detonation combustion is detonated at the location far removed from the spark plug The entire detonation combustion process is completed for a crank angle of 6-7° BTDC [before top dead center], while normal combustion in these conditions occurs much slowly and is concluded when the crankshaft has turned by more than 14° past the TDC (Fig. 20).

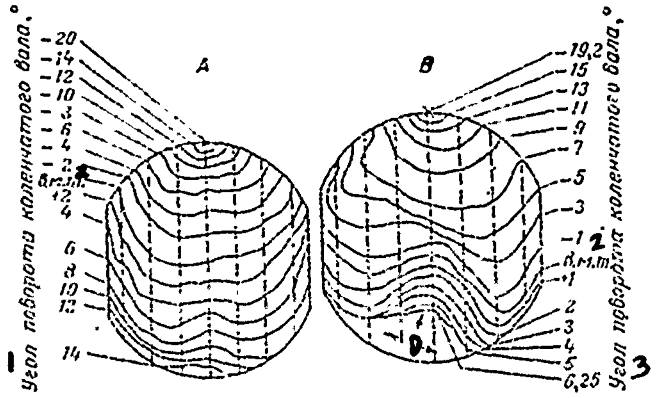

Fig. 20. Propagation of flame front in engine cylinder. The solid lines indicate the instantaneous position of the flame front every 2° of crank angle:

A -- for ignition advance angle 20° before TDC and normal combustion
B -- for ignition advance angle of 19.2° before TDC and combustion with knock
X -- spark
D -- origin of knock

Key: 1 -- Crank angle
2 -- TDC
3 -- Crank angle

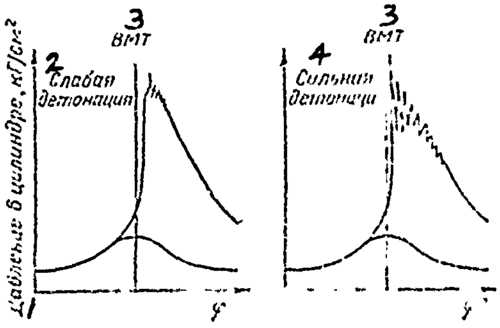

Fig. 21. Typical indicator diagrams of engine with spark ignition when operating with knock

Key: 1 -- Pressure in cylinder, kg/cm^2
2 -- Trace knock
3 -- TDC
4 -- Strong knock

In favor of the multi-stage ignition of the unburned portion of the working mixture is the fact that the C-C and C-H bands characteristic of hydrocarbon flames disappear in the emission spectrum of the flame in the detonation zone. This fact shows that the hot flame develops in this case not in the initial air-hydrocarbon mixture, but in its transformation products containing principally CO. Absorption spectra were used in detecting organic peroxides and aldehydes, and, finally, excited formaldehyde molecules specific for cold flames in the mixture prior to detonation ignition [27].

It was established that introducing small amounts of diethylperoxide ($C_2H_5OOC_2H_5$) or ethylhydroperoxide (C_2H_5OOH) into a combustion chamber causes very intense detonation. Abrupt detonation is caused by introducing acetylhydroperoxide (CH_3COOH). Organic peroxides similar to acetylhydroperoxide were detected in the last portion of the working mixture in an engine prior to the onset of knocking [detonation], in amounts which are necessary to bring about detonation, based on experiments with pure peroxide [28].

We already noted the external signs of detonation combustion: the characteristic rapping, smoky exhaust, and overheating of engine.

Metallic rapping results from numerous periodic reflections of shock waves from the combustion chamber walls. Pulsations in pressure in the form of several gradually dying sharp peaks are recorded at the end of combustion in the indicator diagrams (Fig. 21). The frequency of the pressure pulsations is approximately the same as the principal frequency of the audible rapping -- of the order of several thousands of Hz. Here, in the event of detonation we hear the resounding, high-tone metallic rapping.

Of itself, the pressure rise occurring in the shock wave front does not pose any special danger from the standpoint of the mechanical strength of engine parts, since these pressure peaks act in the form of extremely short impulses lasting for less than 1/1000-th of a second. However, the shock waves with their multiple reflection from walls can mechanically "strip" the oil film from the liner surface, which leads to increased wear of cylinders and piston rings. Moreover, the vibrational nature of loading on the piston when detonation is present can cause the antifriction layer in the crankpin bearings to break down [18].

As the result of the high rate and explosive nature of combustion when detonation occurs, some of the fuel and the intermediate combustion products are "scattered" through the chamber volume, mix with the end combustion products, and are unable to burn completely. A consequence of the incomplete combustion of the mixture in the event of detonation is an increase in exhaust smokiness.

Table 12. Effect of knock on cylinder wear (in microns) [30]

Условия испытаний 1	Средний макси-мальный износ 2	Средний износ в верхнем поясе 3	Средний износ по всем поясам 4
Работа с детонацией 5			
в течение 100 ч			
I этап 6	11,0	5,0	2,7
II этап 7	13,3	5,3	2,5
в течение 200 ч 8			
I этап 6	15,4	9,7	4,6
II этап 7	21,1	10,9	4,8
Работа без детонации 9			
в течение 100 ч	4,6	2,4	1,8
I этап 6	4,1	1,1	1,3
II этап 7			
в течение 200 ч 10	8,1	4,1	3,1
I этап 6	5,5	2,0	2.9
II этап 7			

Key: 1 -- Test conditions
2 -- Maximum wear
3 -- Mean wear in upper zone
4 -- Mean wear over all zones
5 -- Operation with knock for 100 hours
6 -- Stage I
7 -- Stage II
8 -- operation for 200 hours
9 -- Operation without knock for 100 hours
10 -- operation for 200 hours

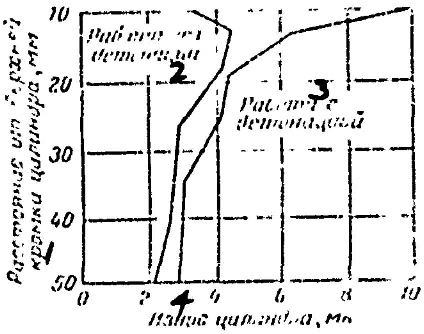

Fig. 22. Radial cylinder wear in the running of an engine [16]
Key: 1 -- Distance from top edge of cylinder, mm
2 -- Operation without knock
3 -- Operation with knock
4 -- Cylinder wear, microns

The main danger of detonation lies in the increased removal of heat from the burned gases into the combustion chamber walls and the piston head owing to the higher temperatures in the detonation wave and the increase in the heat transfer coefficient resulting from the separation of the boundary layer in the colder gas [18].

Increased heat transfer to the walls leads to engine overheating and can cause local damage to the surfaces of the combustion chamber and the piston head initially expressed in the appearance of small pits on the metal surface. Often, first the edges of the gasket between the cylinder and the head break down, ending in the scorching of the gasket. The location of these damaged areas in places quite specific for a given engine is characteristic, the places depending on the configuration of the combustion chamber, which is associated with zones of the predominant initiation of detonation and the conditions of shock wave reflection from chamber walls [18].

It must be noted that even before any visible signs of breakdown appear, running an engine with detonation leads to greater wear of parts [29]. Thus, Table 12 presents the results of a study [30] of the effect of detonation on cylinder wear. Experiments were conducted on a six-cylinder engine in such a way that three cylinders function with detonation, and three -- without. After 200 hours of testing, the second stage was reached, during which time the three cylinders previously operating without detonation [knocking] were switched to the detonation regime, and vice versa. The studies show that when an engine is operated with detonation, In cases when no emergency breakdowns are observed its service life is shortened by 1.5-3 times.

The arrangement of the worn areas along the cylinder height can be seen from the data given in Fig. 22. They indicate that prolonged operation of an engine with detonation is completely impermissible.

The main assumptions of the peroxide theory of detonation explain the effect of various factors on the occurrence of detonation combustion in an engine and assist in outlining ways of controlling this phenomenon.

According to the peroxide theory of detonation, the temperature and pressure rise in engine cylinders must promote faster formation of peroxide compounds and more rapid attainment of critical concentration leading to detonation. An increase in the residence time of the last fuel portions in the compression chamber must also lead to the formation of critical peroxide concentrations and to the initiation of detonation.

These assumptions explain quite well the effect on the initiation of detonation combustion of indicators such as the engine compression ratio, combustion chamber shape, cylinder diameter, the materials used in making the pistons and cylinder blockhead, the presence of carbon deposits, the ignition advance, the crank rpm, the ambient air temperature and humidity, mixture composition, coolant temperature, and so on [31-35].

Detonation in an engine with an increased-diameter cylinder, under all otherwise equal conditions, occurs faster, since the conditions of heat removal deteriorate in this engine.

The shape of the combustion chamber must be such that it is free of areas significantly removed from the ignition source and so that the optimum removal of heat from the portion of the working mixture which is burned last is ensured.

Aluminum piston and cylinder blockhead remove heat better than cast-iron pistons and cylinder block head, and so the conditions for detonation to begin are less favorable in engines with aluminum pistons and cylinder blockhead.

Carbon deposits in a combustion chamber hinder the removal of heat and thus promote detonation.

When the crankshaft rpm is increased, the residence time of fuel in a chamber before combustion is shortened through an increase in the rate of flame front propagation, which leads to lowering of the end concentrations of peroxide compounds and hinders the initiation of detonation.

Detonation in an engine weakens or disperses entirely when there is a reduction in the ignition advance owing to the fact that the temperature and pressure of gases in the engine cylinder are thus lowered and less time remains for peroxide compounds to be formed.

A way of preventing detonation in an engine is to use a fuel that has adequate chemical resistance under combustion chamber conditions, that is, exhibits the requisite antiknock properties.

Uncontrolled Ignition

Earlier it was noted that improvements in automotive carburetor engines have followed the approach of increasing the liter capacity and reducing the specific weight. This is achieved by increasing the compression ratio, filling cylinders more completely with the working mixture, and increasing the crankshaft rpm. The rise in the amount of heat given off in the engine combustion chamber per unit time and the use of more compact chambers with overhead placement of valves leads to a considerable rise in the total thermal stresses in parts, and in several cases -- local overheating of exhaust valves, spark plugs, gasket edges, and combustion chamber surfaces [36].

On the other hand, with a rise in the compression ratio and with higher thermal stresses in an engine, the working mixture at the end of the compression stroke becomes more and more "prepared" for ignition.

The appearance of "hot spots" in the combustion chamber causes the spontaneous ignition of the working mixture, regardless of the spark timing. This phenomenon, causing a disruption in the normal combustion process, is called surface ignition or glowing ignition.

Surface ignition via its nature differs fundamentally from detonation ignition, although these phenomena are closely interrelated in automotive engine working conditions. However, the combustion of a mixture after glowing ignition occurs at normal rates and may not be accompanied by detonation.

The ignition of working mixture from a "hot point" before the appearance of the ignition spark acts on the combustion process just as setting an earlier spark timing, that is, it promotes detonation. On the other hand, detonation combustion causes a considerable rise in the temperature conditions in an engine and promotes the appearance of "hot spots" in the combustion chamber and glowing ignition. Thus, glowing ignition and detonation are intimately related and often both phenomena appear in an engine at the same time, but the mechanisms of these processes and ways of controlling them differ widely.

External signs of glowing ignition and the consequences to which it leads depend on factors such as the number and size of the ignition sources, and the phase of the initiation, intensity, and stability of this phenomenon. The abundance of signs of glowing ignition and the lag of adequate study given to the mechanism of the processes that occur led to the need to classify all the observed disturbances by purely external symptoms [37].

All kinds of surface ignition are divided, by their phase of appearance, into premature ignition (before the appearance of the ignition spark) and subsequent ignition (after the appearance of the ignition spark).

Premature glowing ignition, depending on the intensity and stability of its occurrence, is divided into noiseless, stable, audible, and self-accelerating.

Subsequent glowing ignition based on these same symptoms is divided into noiseless and glowing ignition accompanied by a strong dull rapping. The combined periodic occurrence of glowing ignition and detonation accompanied by sharp cracking sounds is called "wild" rapping. Special groups are used to classify glowing ignition causing continuation of the engine operation after ignition has been turned off in full load or in idling, rough engine operation due to glowing ignition but not accompanied by rapping, and noisy ignition occurring when a heated engine is started up.*

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* All these terms are taken from the foreign literature. (Editor's note)

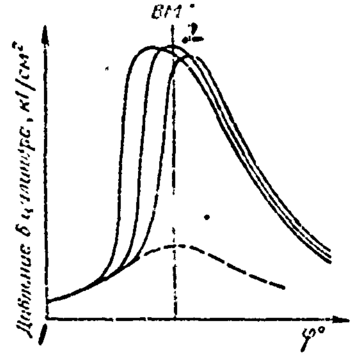

Fig. 23. Indicator diagrams of several successive engine cycles with sharply pronounced premature ignition from incandescent surface
Key: 1 -- Pressure in cylinder, kg/cm^2
2 -- TDC

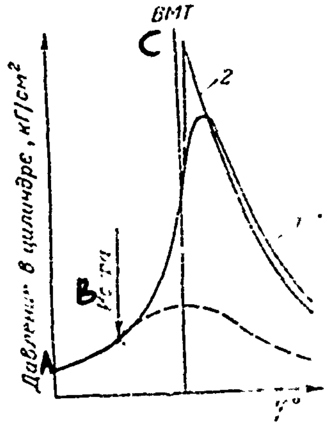

Fig. 24. Composite indicator diagrams of spark-ignition engine:
1 -- at normal combustion
2 -- with subsequent self-ignition [22]
Key: A -- Pressure in cylinder, kg/cm^2
B -- Spark
C -- TDC

This classification, in spite of its fairly frequent use in the literature, has significant disadvantages. All the disturbances considered have a common cause -- the ignition of a working mixture from a "hot spot," therefore one kind of disturbance can shade into another when there is a limited change in the conditions in the combustion chamber. External manifestations of glowing ignition taken as the basis of the classification, are sometimes difficult to differentiate owing to the overall noise level of engine operation. However, the consequences of glowing ignition within the framework of this classification can be considered quite precisely.

Premature ignition of a working mixture is accompanied by a drop in engine power due to an increase in power outlay in compressing the combustion product (Fig. 23). However, the main danger in premature ignition involves the increase in heat removal to the walls owing to a rise in the time the burning gases spent in cylinders at high temperatures [18, 22].

The initiation of ignition foci after flame begins to spread from the spark leads to a rise in the rate of pressure increase to 8-10 kg/cm^2 per degree, instead of the usual 2 kg/cm^2 per degree in normal combustion. Indicator diagrams take on the appearance of sharp spikes (Fig. 24); here

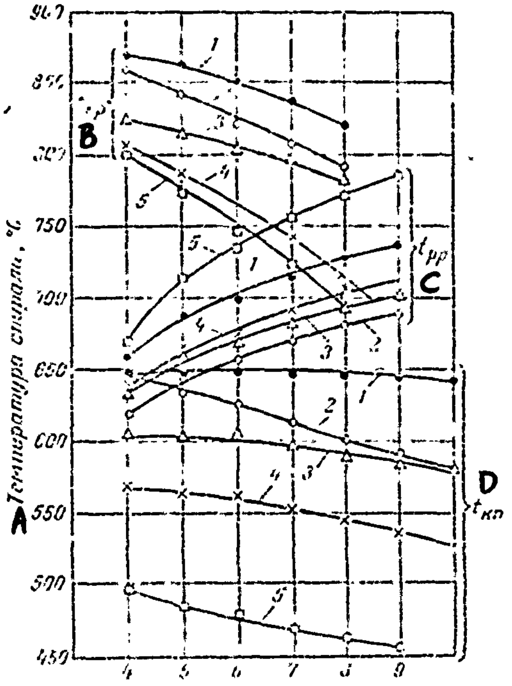

Fig. 25. Glowing Properties of hydrocarbons [36]:

1 -- benzene
2 -- isooctane
3 -- isopropylbenzene
4 -- diisobutylene
5 -- methyl alcohol

Key: A -- Temperature of spiral
B -- t_{cr}
C -- $t_{o.g}$
D -- $t_{i.g}$

the maximum pressures in the combustion chamber rise sharply. Most often a disturbance of the kind called "rumbling" is encountered. It develops usually when an engine passes over to full-open throttle regimes after prolonged operation at low loads.

Thus, glowing ignition disturbs the normal progression of the combustion process, makes it uncontrolled, and leads to a power loss and deterioration of engine operating economy. Intense glowing ignition causes a burn-through and mechanical failure of pistons, flattening of piston rings, scorching of the edges of pistons and valves, breakdown of bearings, fracturing of connecting rods, and fracturing of crankshafts. Recently, foreign specialists have evaluated the control of premature ignition in engines with high compression ratios as a problem that is more important than controlling detonation [knocking].

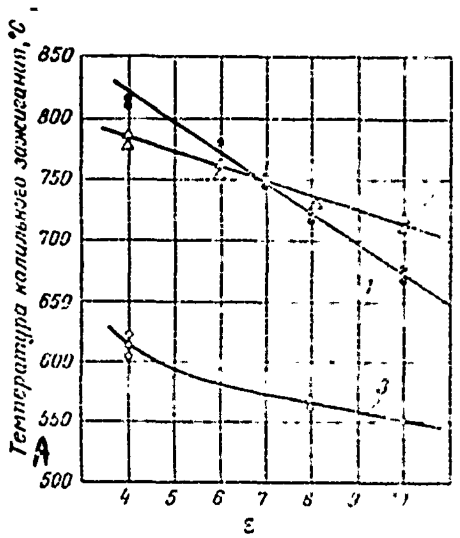

Fig. 26. Resistance of isooctane (1), benzene (2) and methyl alcohol (3) against glowing ignition of heated spiral [90] ($\alpha = 1$; temperature of mixture and air is 50° C)

Key: A -- Temperature of glowing ignition

Table 13. Relative estimate of glowing resistance of hydrocarbons when ignited by heated surfaces [36] (resistance to glowing ignition decreases from 1 to 4)

Углеводород 1	Относительная оценка по данным различных исследований 2										
Изооктан 3	1	1	2	1	1	1	1	2	1	2	2
Толуол 4	—	—	1	3	2	—	2	1	–	1	1
Бензол 5	2	2	1	2	4	2	4	3	2	3	4
Диизобутилен 6	3	3	3	4	3	—	3	4	3	4	3

Key: 1 -- Hydrocarbon
2 -- Relative estimate based on the data of various studies
3 -- Isooctane
4 -- Toluene
5 -- Benzene
6 -- Diisobutylene

Study of the glowing ignition phenomenon in automotive engines began relatively recently — 15-20 years. However, during this time interesting works were published on the mechanism of the phenomenon as a whole [23-48] and of its individual kinds [49-57], signs of glowing ignition [68-74], and the effect of the quality of fuels and oils [65-68] and of additives [68-74]. Several methods of investigating glowing ignition in engines have been proposed [75-85]. In the USSR, works by A. N. Voinov, D. M. Aronov, M. O. Lerner, Yu. A. Robert, F. V. Turovskiy, N. F. Rumyantsev, and S. G. Nechayev have dealt with glowing ignition [86-96].

It is useful to subdivide all kinds of glowing ignition not by its external manifestation, but by the nature of the ignition source -- into glowing ignition by neutral heated bodies (metallic surface) and by active surfaces (carbon deposits).

Glowing ignition by metallic surfaces is usually studied in an engine into whose combustion chambers spirals heated by electric current have been inserted. The spiral temperature at which glowing ignition appears in the working regime ($t_{o.g}$) or in the idling regime ($t_{i.g}$[i.g = idling glow] and also the self-heating temperature of the spiral in the working regime ($t_{w.r}$) are adopted as the criterion for rating fuel stability.

The results of experiments [36] show that as the compression ratio is increased, the resistance of hydrocarbons to glowing ignition caused by metallic surfaces becomes less (Fig. 25).

The effect of the conditions in which the resistance of hydrocarbons to glowing ignition caused by metallic surfaces are determined is so major that for some hydrocarbons, when these conditions are changed their relative rating can also change (Table 13).

These data show that most studies take note of the highest resistance of isooctane to glowing ignition, though in several investigations toluene and benzene have shown greater resistance.

The variation in the relative rating of hydrocarbons by their tendency to undergo glowing ignition as a function of the compression ratio is well illustrated by the data in Fig. 26. When the compression ratio is less than 7, isooctane exhibits greater resistance to glowing ignition than benzene, and for a compression ratio greater than 7 — benzene, in contrast, is more resistant.

Most investigators agree that a gain in the knock resistance of fuels is accompanied by a rise in their resistance to glowing ignition caused by heated metal surfaces. Blends of isooctane with heptane have a linear relationship between these indicators, but a strict correlation has not been found for other hydrocarbons and fuels, although a general tendency of an increase in glowing resistance with increase in octane numbers has been observed. The presence of antiknocks in gasoline affects the glowing resistance only to the extent that it causes a rise in the octane number [36].

A method based on the IT-9 laboratory single-cylinder stand intended for octane number determination [36] has been proposed to rate the resistance of fuels to glowing ignition caused by heated metal surfaces. Glowing ignition is caused by a spiral which is heated with an electric current. The temperature at which glowing ignition appears in the standard regime (600 rpm, $\alpha = 1$, and mixture temperature 50° C) for a compression ratio corresponding to the standard intensity of detonation [knocking] according to the octane number determination method.

Glowing resistance can be expressed, by this method, in terms of the isooctane equivalent IE:

$$IE = (t^F_{i.g}/t^I_{i.g})\cdot 100 \quad ,$$

where $t^F_{i.g}$ is the temperature of glowing ignition in the idling regime of the rated fuel and $t^I_{i.g}$ is the temperature of glowing ignition for isooctane, for the same compression ratio.

The rating of certain fuels by this indicator is given below:

		IE
Isooctane		100
Benzene		106
Isopropylbenzene		98
Diisobutylene		90
Methylalcohol		75
Blends of isooctane and n-heptane		
80%	20%	95
60%	40%	86
40%	60%	83
20%	80%	78
Blends of isooctane and nitropropane		
95%	5%	93
90%	10%	87
80%	20%	80
Nitropropane		68

Based on these data, isooctane and benzene can be recommended as the upper reference fuels in rating glowing ignition by heated metal surfaces, and methyl alcohol, n-heptane, and nitropropane can be recommended as the lower references [92]. Studies show that the glowing resistance of nitropropane is much below that for isooctane and remains constant over a wide range of compression ratios. The glowing resistance of blends of isooctane and nitropropane decreases with increase in nitropropane content in the blend. This relationship is preserved for both the idling regime as well as the operating regime. The use of nitropropane as the lower reference instead of n-heptane in blends with isooctane expands the limits of the rating scale [92].

In recent years major success has been achieved in controlling glowing ignition caused by metal surfaces by design improvements in combustion chambers, using "cold" spark plugs, sodium-cooled valves, and so on, however problems of the glowing resistance of fuels and ways of increasing it continue to be studied by many investigators.

More experimental studies dealt with glowing ignition caused by carbon deposits than glowing ignition caused by metal surfaces. But the very phenomenon of glowing ignition caused by carbon deposits is much more difficult to study owing to the complexity, instability, and brevity of the ongoing processes.

At the present time fairly extensive material on the effect of various regime and operating factors on glowing ignition caused by carbon deposits has been accumulated.

It has been shown unambiguously that an increase in the compression ratio causes a rise in the intensity of glowing ignition in all rating indicators. As a rule, glowing ignition occurs in full loads and its intensity drops with decrease in the load, obeying a near-linear function.

The intensity of glowing ignition rises when there is some enrichment in the combustible mixture and with the adjustment of later ignition. The appearance of glowing ignition is promoted by all factors that increase the temperature conditions in an engine. These include a higher rpm and higher air and fluid temperature in the cooling piston. The increase in humidity causes a decrease in the intensity of glowing ignition.

Based on these studies, the scheme for the initiation of glowing ignition caused by carbon deposits is represented as follows. The most intense deposit formation is observed in the low-load regime. With the transition to full loads, the temperature of deposit particles adhering to combustion chamber parts and also flaking off and found in the above-piston space begin to rise owing to an increase in the thermal stresses of the cycle. The temperature of deposit particles continually varies as a result of heat exchange with ambient gases. During combustion and exhaust, carbon deposts are heated by hot gases and the deposit temperature rises, while during intake carbon particles are cooled by the fresh mixture. But deposits are not simple "accumulators" of heat arriving from the heated gases. It was found that the carbon deposit substance, at certain temperatures, is capable of reacting chemically with air oxygen, giving off heat. In other words, at certain temperatures carbon deposits can heat up spontaneously, resulting in their temperature attaining values that exceed the ambient temperature. This characteristic of carbon deposit strongly distinguishes it as an ignition source from an "inert" metal surface. In contrast to the latter, carbon deposits are sometimes referred to as "active" surfaces and their ability to ignite a combustible mixture is associated with the "chemical activity" of the deposits.

Certain characteristics of glowing ignition caused by carbon particles are associated with the ability of carbon to heat spontaneously owing to exothermic reactions with oxygen. A heated carbon deposit particle, on absorbing oxygen, causes a reduction in its concentration at the surface, and as a result the mixture at the carbon deposit surfaces becomes over enriched and can pass beyond the limits of ignitability. Therefore the ignition of a mixture by carbon deposits often can occur only at some distance from the surface where the mixture concentration is close to the initial value. Owing to the fact that with increasing separation from an incandescent deposit particle the temperature decreases, the deposit particle must be somewhat higher than the ignition point of the mixture in order for glowing ignition to appear. These correlations are well illustrated by the curves in Fig. 27.

Within the limits of the distance x from the surface of the deposits, the air-fuel mixture is too rich and lies beyond the ignitability limits; on the other hand, at a distance greater than y from the deposit surface the mixture temperature can prove to be lower than is required for its ignition. And only in the zone lying at a distance between y and x from the deposit surface can the mixture satisfy ignitability conditions both as to composition and temperature (cf. Fig. 27).

Thus, glowing ignition caused by carbon deposits, as well as metal surfaces differs appreciably by the role and behavior of the igniting body.

Studies show that the ignition point, rate of combustion and of heating, and also the maximum temperature depend on the composition and temperature of the deposits, the shape and size of deposit particles, their specific heat capacity, chemical activity, heat transfer conditions, and also the composition and temperature of the medium.

One of the main difficulties in studying glowing ignition caused by carbon deposits is the absence of standardized methods of investigating this phenomenon. Differences in these methods sometimes lead to contradictory results in the rating of hydrocarbons and fuels (Table 14).

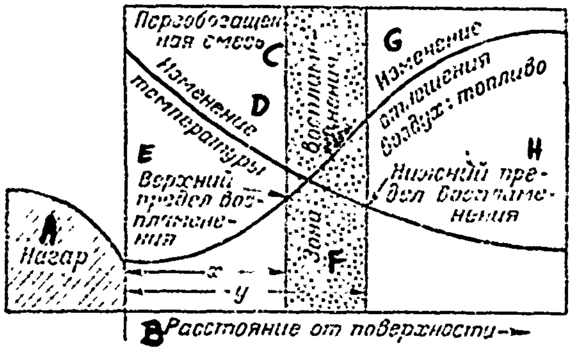

Fig. 27. Change in oxygen concentration in mixture and temperature distribution near incandescent carbon deposit particle [63]

Key: A -- Carbon deposit
B -- Distance from surface
C -- Overrich mixture
D -- Temperature change
E -- Upper limit of ignition
F -- Ignition zone
G -- Change in air:fuel ratio
H -- Lower limit of ignition

Table 14. Relative estimate of glowing resistance of hydrocarbons when ignited from carbon deposits [36] (resistance to glowing ignition decreases from 1 to 5)

Углеводород 1	Относительная оценка по данным различных исследователей 2							
Изооктан 3	1	1	1	1	1	1	1	1
Толуол 4	2	4	3	5	2	3	4	[illegible]
Диизобутилен 5	3	2	2	3	4	2	2	
Бензол 6	4	5	5	4	5	1	5	2
Циклогексан 7	—	3	4	2	3	-	3	-

Key: 1 -- Hydrocarbon
2 -- Relative estimate based on the data of different investigators
3 -- Isooctane
4 -- Toluene
5 -- Diisobutylene
6 -- Benzene
7 -- Cyclohexane

Existing methods differ in factors such as methods of detecting glowing ignition, rating criteria for its intensity, methods of initiating glowing ignition, and test conditions [36].

Without detailing all the characteristics of the proposed methods for rating glowing ignition, which is a subject of a recently published work [96], we know that at the present time it has been shown possible to rate the tendency of fuels to undergo glowing ignition from carbon deposits not only in laboratory conditions, but also in stand and road conditions, and here the resulting data proved to be quite close to each other for a number of hydrocarbons.

Both motor and laboratory methods of rating carbon deposit properties are used in our country in studying glowing ignition caused by deposits. One of the motor methods provides for introducing finely ground deposits into a combustion chamber with a special gun [95]; another is based on the preliminary accumulation of deposits in a chamber for operation in a special regime [96]; and a third method involves recording pulses with the normal operation of a single-cylinder engine [89].

From the standpoint of studying the role of fuel in glowing ignition caused by deposits, the most detailed studies have been made by D. M. Aronov and Yu. A. Robert. They developed and tested an original method of examination on a single-cylinder engine of the IT-9 stand. Essentially, the method consists in the accumulation of deposits in the low-temperature regime and in recording the number of bursts of glowing ignition when carbon deposits are ignited in the high-temperature regime. The main parameters of the method of rating the tendency of fuels to undergo glowing ignition caused by deposits on the IT-9 stand engine were as follows [96]:

	Carbon deposit accumulation regime	Carbon deposit ignition regime
n, rpm	1200 ± 30	1200 ± 30
Compression ratio	6.0	7.0
α	0.6	1.0
θ, °	25 ± 1	TDC
Temperature, °C		
of air-fuel heating mixture	100 ± 1	155 ± 5
of air heating	40 ± 2	52 ± 2
of coolant	65 ± 5	95 ± 5
of crankcase oil	60 ± 5	65 ± 5
Duration, minutes	30	Until the readings of glowing cycles stop

The tendency of fuel to glowing ignition based on this method can be rated in different ways: by the property of the deposits and by the ability of the fuel to be ignited thereby. The method permits deposits to be accumulated for the same fuel (carbon deposit-forming fuel) and for the deposits to be burned with another (igniting fuel). If the deposits are accumulated with the test fuel and all the deposits are burned with some reference fuel, the resulting data provide a comparison between the glowing activity of the deposits. On the other hand, by using the same reference fuel for accumulating the deposit and burning the deposit with test fuels, differences between fuel tendencies to be ignited by the deposits can be rated. And, finally, an overall rating of the glow resistance of fuel is possible in which deposit accumulation and burning is carried out with the test fuel.

Accordingly, the authors of the method proposed rating the glow tendency of a fuel by using three-dimensional indicators, called glow numbers.

1. The deposit glow number, DGN, characterizes the ability of deposits to cause glowing ignition:

$$\mathrm{DGN} = (K_{t/r}/K_{r/r})\cdot 100 \ .$$

2. The ingition glow number, IGN, characterizes the tendency of a fuel to be ignited by reference fuel-produced deposits:

$$\mathrm{IGN} = (K_{r/t}/K_{r/r})\cdot 100 \ .$$

3. The overall glow number, OGN, characterizes the tendency of a fuel to be ignited by its own deposits:

$$\mathrm{OGN} = (K_{t/t}/K_{r/r})\cdot 100 \ ,$$

where K is the number of cycles with glowing ignition, the superscript indicates the type of the carbon deposit-forming fuel, the subscript indicates the type of the igniting fuel (t = test fuel, r = reference fuel).

With increased tendency of a fuel or deposit to undergo glowing ignition, the glow numbers correspondingly rise. The tendency of benzene containing 0.82 g TEL per kg of fuel to glowing ignition is taken as 100 glow points.

It must be noted that in the United States TIB blends -- isooctane with benzene containing 0.8 ml TEL per 1 of fluid (octane number 115) -- are used in rating the tendency of fuels to glowing ignition. In these blends the resistance of isooctane is taken as 100 points, and that of

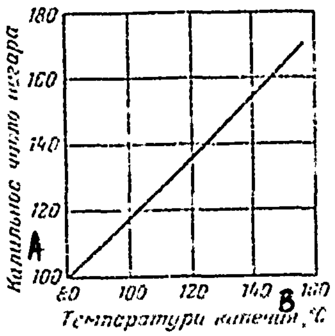

Fig. 28. Effect of boiling points of aromatic hydrocarbons on the glowing activity of carbon deposits
Key: A -- Glow number of carbon deposits
B -- Boiling point, ° C

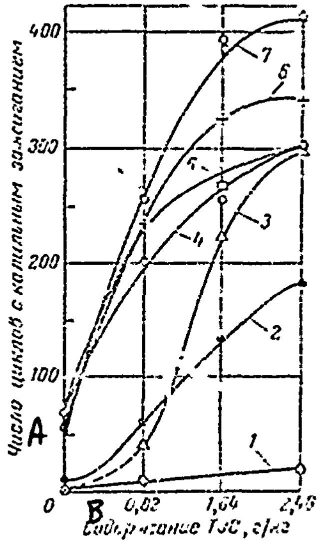

Fig. 29. Effect of TEL content in fuel on the glow activity of carbon deposits [96]:
1 -- glow forming agent -- isooctane, ignition agent -- benzene
2 -- diisobutylene - benzene
3 -- thermal cracking gasoline - benzene
4 -- benzene - benzene
5 -- catalytic reforming gasoline
6 -- catalytic cracking gasoline
7 -- toluene - benzene
Key: A -- Number of cycles with glowing ignition
B -- TEL content, g/kg

structure of aromatic hydrocarbons and their molecular weight are decisive. High-molecular aromatic hydrocarbons form the most active deposits. As the boiling points of aromatic hydrocarbons rise, the glow numbers of their deposits increase linearly (Fig. 28).

Benzenes prepared by drastic-regime catalytic reforming and by the catalytic cracking of heavy crude, as we can see from the above-presented data, have similar deposit glow numbers (117.0 and 115.0), with different total content of aromatic hydrocarbons (59.5 and 22 percent, respectively), but with identical content of C_9 and higher aromatic hydrocarbons. These data also indicate the dominant role of high-molecular aromatic hydrocarbons in forming active deposits.

The glow activity of carbon deposits depends strongly on the presence of antiknock additives in a gasoline. The increase in the glow numbers of deposits when tetraethyl lead is added varies as a function of the hydrocarbon composition of the fuel (Fig. 29).

The greatest effect of tetraethyl lead is observed in fuel containing considerable amounts of aromatic hydrocarbons. And the greatest increment in the glow numbers of carbon deposits occurs for small additions of tetraethyl lead [96].

The presence of tetraethyl lead in fuel affects the composition and properties of the deposits formed. The highest ignition point is shown by deposits consisting of pure carbon (550-600° C). A small addition to hydrocarbon deposits of oxides or halogen compounds of lead (deposits of ethyl fuels) leads to a sharp drop in the ignition point down to 200-300° C, which is very appreciable for combustion chamber conditions.

Engine experiments showed that deposits having lower ignition points cause more intense glowing ignition. It was noted that the presence of lead leads to a rise in the temperature and rate of carbon deposit combustion. At the same time lead promotes the more complete and more rapid combustion of carbon.

The carbon deposit composition is determined not only by the deposit ignition point, but also by the rate at which deposits react with oxygen, that is, the rate of self-ignition [autoignition]. Recently, this property of deposits has been studied very closely using special thermographic methods. A direct relationship has been established between the intensity of glowing ignition and the rate of exothermic reactions occurring in deposits [96].

The tendency of various fuels to ignite with the same "reference" deposits varies within narrower limits than the glowing activity of carbon deposits. This is evident when we compare the glowing number for the ignition of hydrocarbons and gasolines [96]:

	IGN*
Isooctane	21.9
Diisobutylene	23.1
Methylcyclohexane	27.9
o-Xylene	40.8
Isopropylbenzene	78.8
Toluene	81.0
Benzene	100.0
Gasolines	

[Continued on following page]

[Continued from preceding page]

AI-93 (nonethyl)	35.0
AI-93 (ethyl)	31.7
ordinary-regime catalytic reforming	38.7
drastic-regime catalytic reforming	58.0

* IGN = ignition glow numbers

Aromatic hydrocarbons have the largest ignition glow numbers. The ignition glow numbers of gasolines then depend on the content and structure of aromatic hydrocarbons. As the molecular weight of an aromatic hydrocarbon is increased, its ignition glow number becomes smaller.

It is customary to explain the difference in ignition glow numbers of hydrocarbons by the different combustion rates and flame temperatures.

Robison [85] introduced a rod pressed from carbon and lead oxide into the combustion chamber to estimate the deposit heating temperature when various fuels are burned. The rod temperature served as an indicator of the ability of fuels to heat up carbon deposits (Fig. 30).

The most rapid heating of deposits is achieved when operating with benzene; a temperature rise that is slowest is observed in the combustion of isooctane. These results correspond to the relative rating of these hydrocarbons by their tendency to undergo glowing ignition. Similar results were obtained also in a determination made of the combustion rates of various hydrocarbons (Table 15).

The addition of tetraethyl lead to gasolines and hydrocarbons has practically no effect on their ignition proneness.

The overall glow numbers of various fuels vary with wide limits, roughly corresponding to the limits of change in the glow numbers of deposits produced with these same fuels:

	OGN*
Isooctane	0.0
Isooctane + TEL (0.82 g/kg)	0.0
Methylcyclohexane	0.0
Methylcyclohexane + TEL (0.82 g/kg)	2.5
Diisobutylene	0.0
Diisobutylene + TEL (0.82 g/kg)	8.5
Benzene	35.0
Benzene + TEL (0.82 g/kg)	100.0

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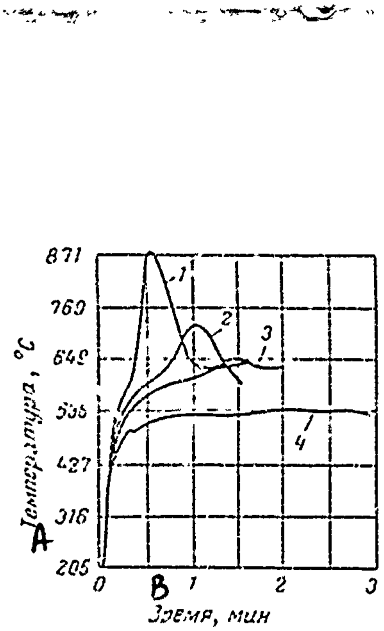

Fig. 30. Change in temperature of carbon deposit tablet when engine is operated on various fuels [85]:
1 -- benzene
2 -- toluene
3 -- diisobutylene
4 -- isooctane
Key: A -- Temperature
B -- Time, minutes

[Continued from preceding page]

Toluene + TEL (0.82 g/kg),	113.0
o-Xylene+ TEL (0.82 g/kg)	124.0
Isopropylbenzene + TEL (0.82 g/kg)	134.0
Alkylate	0.0
Gasoline	
ordinary-regime catalytic reforming + TEL (0.82 g/kg)	39.5
drastic-regime catalytic reforming	26.0
as above + TEL (0.82 g/kg)	54.0
A-76 (containing TEL)	13.5
AI-93 (not containing TEL)	23.5
AI-93 (containing TEL)	41.0

[* OGN stands for overall glow numbers.]

Overall glow numbers depend on the same factors as the glow numbers of deposits; they increase with increase in the aromatic hydrocarbon content, with increase in the molecular weight of aromatic hydrocarbons, and with higher TEL concentration in fuel.

Table. 15. Combustion time of various hydrocarbons for the same knock resistance [85]

Топливо 1	Весовое отношение воздуха к топливу 2	Угол опережения зажигания θ, °ПКВ 3	Общая продолжительность сгорания, °ПКВ 4
$n = 1200$ *об/мин* 5			
Бензол 6	11,6	26	53
Толуол 7	11,6	31	55
Диизобутилен + ТЭС (1,55 *г/кг*) 8	13,8	30	59
Изооктан + ТЭС (1,55 *г/кг*) 9	12,9	34	59
$n = 2400$ *об/мин* 5			
Бензол 6	11,7	30	55
Толуол 7	11,4	33	59
Диизобутилен + ТЭС (1,55 *г/кг*) 8	13,5	34	61
Изооктан + ТЭС (1,55 *г/кг*) 9	13,1	36	65

Key: 1 -- Fuel
2 -- Weight ratio of air to fuel
3 -- Ignition advance angle, θ, ° crank angle
4 -- Total combustion time, ° crank angle
5 -- rpm
6 -- Benzene
7 -- Toluene
8 -- Diisobutylene + TEL (1.55 g/kg)
9 -- Isooctane + TEL (1.55 g/kg)

Thus, the glow properties of carbon deposits have a decisive effect on the overall rating of a fuel's tendency to glow ignition and determine the probability of this process occurring in an engine and its intensity. This conclusion is vital, since it enables us to determine the main direction in controlling glowing ignitions -- modifying the properties of the deposits formed aimed at reducing its glow activity [96].

Changes in deposit composition and properties can be achieved by introducing special additives into fuels and oils. Various phosphorus compounds (phosphates, phosphites, and phosphanates), and compounds of boron, bromium, chlorine, silicon, chromium, cobalt, barium, zinc, calcium, and so on have been investigated as antiglow additives [97-102]. Phosphorus-containing compounds were found to be the most effective for fuels [69-74].

The action of phosphorus additives is related to their ability to react with the combustion products of tetraethyl lead, forming lead phosphates. Deposits containing, instead of lead oxides, lead phosphates have higher glow (ignition) temperatures:

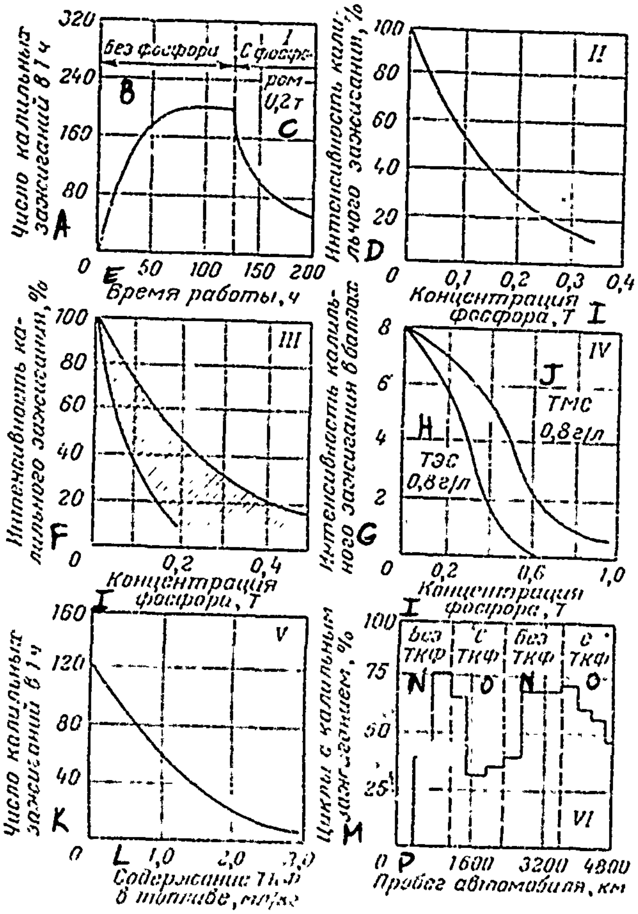

Fig. 31. Effectiveness of phosphorus compounds in suppressing glowing ignition:

I -- based on the data in [72]

II -- based on the data in [83]

III -- based on the data in [72], the zone of values for phosphorus compounds of various compositions is shaded

IV -- based on the data in [102]

V -- based on the data in [36]

VI -- based on the data in [69]

Key: A -- Number of glowing ignitions per hour

B -- Not containing phosphorus

C -- Containing 0.2 T phosphorus [T is the theoretically required amount of phosphorus to convert lead contained in gasoline to the orthophosphate $[Pb_3(PO_4)_2]$

D -- Intensity of glowing ignition

[Key continued on following page]

[Key continued to Fig. 31 on preceding page]:
E -- Running time, hours
F -- Intensity of glowing ignition
G -- Intensity of glowing ignition in scale divisions
H -- TEL, 0.8 g/l
I -- Concentration of phosphorus, T
J -- TML, 0.8 g/l
K -- Number of glowing ignitions per hour
L -- Content of TCP [tricresylphosphate] in fuel, ml/kg
M -- Cycles with glowing ignition
N -- Not containing TCP
O -- Containing TCP
P -- Vehicular travel, km

Additives	Deposit composition	Glow temperature, °C
None	C	550
TEL + scavengers	C + PbO	300
	C + $PbBr_2$	200
	C + $2PbO \cdot PbBr_2$	230
TEL + scavenger + phosphorus compounds	C + $Pb_3(PO_4)_2$	460
	C + $3Pb_3(PO_4)_2 \cdot PbBr_2$	350
TEL + scavenger + boron compounds	C + $PbO \cdot B_2O_3$	340

The efficiency of phosphorus additives and, in particular, tricresylphosphate (TCP) was checked in laboratory, stand, and road tests (Fig. 31). The tests revealed also certain characteristics of TCP use associated with deposit formation, octane requirements of the fuels used, and so on. However, these data are highly contradictory. Evidently, adding TCP still somewhat increases overall deposit formation. The data of the several investigators are directly contradictory as to the changes in knock resistance requirements of an engine. Thus, Geoffrey [69] noticed a decrease in requirements, when TCP was present, of as much as 8 octane points, while Fleming [61] found a rise of 1.7 octane points in the requirements when TCP was added in the amount of 0.2 T*. Obviously, the rise in the requirements is related to the volumetric action of the deposits, and the decrease is associated with the catalytic effect of phosphorus compounds contained in deposits on preflame reactions leading to detonation. The predominance

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* T is the theoretically required amount of phosphorus to convert the lead contained in gasoline to the orthophosphate [$Pb_3(PO_4)_2$].

of any given factor caused by the design characteristics of combustion chambers, the additive concentrations used, and so on can evidently affect test results.

Phosphorus additives have found very wide industrial use, are being produced by a number of companies, and are used in automotive gasolines in the United States and several other countries [97]. At the present time phosphorus additives are used abroad under various trade names. These additives include bis-(beta-chloroisopropylthiophophate), methylphenylphosphates, trimethylphosphate, cresyldiphenylphosphate, and so on. Their use in the amount of 0.2 T. Total consumption of phosphorus additives in the United States exceeded 16,000 tons already in 1966 [104].

Phosphorus additives have not found use thus far in the USSR, though study of their efficiency and characteristics of application is underway. It must be expected that an increase in compression ratio in prospective domestic automotive engines and the use of highly aromatized products of catalytic reforming will lead already in the near future to the necessity of taking effective measures in controlling glowing ignition.

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CHAPTER THREE

ANTIKNOCK PROPERTIES OF GASOLINES

Rating Methods

Various methods have been proposed for rating the antiknock properties of automotive gasolines; they are based on the testing of fuels on nonmotor stands (bombs and adiabatic compression machines), single-cylinder laboratory and full-sized multicylinder engines in stand and road conditions. Attempts to set up a reliable reference method for rating the antiknock properties of gasolines on nonmotor stands have thus far not borne positive results [1]. Most methods for determining the antiknock properties of fuels are based on their combustion in engines.

Virtually all characteristic manifestations of the knock combustion of gasolines in engines are used in rating knock: increase in the rate of combustion and in the pressure rise, increase in the temperatures of gas and combustion chamber walls, vibration of gas and the engine housing, appearance of specific products of preknock reactions, change in the character of the exhaust, abrupt decrease in power, and so on. Some of these signs of knocking are used only for research purposes, while others are used for the quantitative measurement of the knocking intensity in control instruments and stands [1-11].

Methods based on temperature and pressure measurements gained the greatest acceptance in measuring the knocking intensity. Measuring the temperature of the last portion of a charge proved to be quite complex and a poorly suitable method of rating knock. The method of measuring the mean temperature of the combustion chamber walls gained practical application; on the basis of this technique, the so-called temperature method of rating the knock resistance of aviation gasolines was developed.

Pressure measurement in the combustion chamber is most widely used in modern methods for the quantitative rating of detonation. Numerous studies showed that the mechanical vibrations of an engine, acoustic vibrations, and the vibrations of gas and flame in engines in the event of knocking coincide in frequency and, being a consequence of detonation combustion, can be used for its detection and for the quantitative measurement of its intensity. An instrument measuring the rate of pressure rise in the engine combustion chamber by a mechanical method (the so-called "Midgley needle") won the widest acceptance. At the present time, more advanced electrical pressure transducers (piezoquartz, induction, magnetostriction, capacitive, strain gage, and so on) have been developed; their application permits boosting the precision of determinations [1].

The first single-cylinder stand with variable compression ratio was invented by G. Ricardo in the early 1920's, and the first method of rating the knock resistance of fuels by the so-called "critical" or "most useful" compression ratio at which audible knocking began was based on this stand [1]. Thus, even in the first method of rating the knock resistance of gasolines, detonation was brought about by increasing the compression ratio. Subsequently, virtually all parameters of the engine operating regime (throttling, supercharging, rpm, mixture composition, ignition advance, temperature conditions, and so on) were used to initiate detonation, however thus far varying the compression ratio is the main factor in producing conditions of knock combustion in laboratory methods of rating antiknock properties of gasolines.

At the present time, special stands with single-cylinder engines are used in rating the antiknock resistance of automotive gasolines in laboratory conditions. In the USSR, the Motor Method (GOST [State Standard] 511-46) was used up until 1949 in rating the octane numbers of automotive gasolines. In 1949, the aviation industry developed [1] the design and organized the series production of the IT9-2 domestic single-cylinder stand for fuel testing. Later, owing to changes in petroleum refining technology and the production of new engine models in the USSR, as well as in other countries, it became necessary to use a method of rating octane numbers that was less stringent than the Motor Method. In 1959, a domestic stand for the Research Method of determining octane number was developed on the basis of the IT9-2 stand; it was designated as the IT9-6 stand [1, 12].

The next stage in improving domestic methods of rating octane numbers was the invention of the DP-60 electronic detonation meter instead of the electromechanical transducer with a sliding needle. Use of the electronic detonator significantly increased the precision of octane number determination [13, 14].

In recent years, a new general-purpose stand intended for the determination of octane numbers by the Motor as well as by the Research Method was developed and thoroughly tested -- the UIT-65 [1]. The new stand is equipped with automatic electronic devices for maintaining a constant regime.

At the present time, octane numbers of automotive gasolines on laboratory stands are determined by two methods -- the Motor (GOST 511-66) and the Research (GOST 8226-66) methods.

The IT9-2 and IT9-6 laboratory stands are of the same type; they consist of a single-cylinder engine, asynchronous electric motor, a control panel, columns for maintaining constant humidity of intake air, a device for measuring knock, and auxiliary equipment. The single-cylinder piston, four-stroke carburetor internal combustion engine with liquid thermosiphon-evaporative cooling, and with a special device for varying the compression ratio (from 4 to 10) consists of crankcase, cylinder and piston, crank-connecting rod mechanism, and also lubricating and cooling systems /15/.

The tendency of a test gasoline to knock is rated by comparing it with reference fuels whose knock resistance is known in advance. As a rule, the reference fuels are pure individual hydrocarbons or other compounds, whose names are used to designate the corresponding "number" -- toluene, benzene, xylene, aniline, ethyl, and so on /1/. Currently, the so-called octane number is used most widely in rating knock resistance. In its determination, the reference fuel is prepared by blending two individual hydrocarbons. One of them -- isooctane (2,2,4-trimethylpentane) -- detonates only at a high compression ratio and its knock resistance is taken as 100 octane points. The other hydrocarbon -- n-heptane -- exhibits poor antiknock properties and its octane number is taken as zero. Blends of isooctane and heptane in various ratios exhibit different knock resistance; it is characterized by octane numbers from 0 to 100.

The octane number of a gasoline is determined as follows. For operation with the test gasoline, knocking of a specific intensity is caused to appear by varying the engine compression ratio. Then a reference blend of hydrocarbons is selected such that, at the same compression ratio, it detonates with the same intensity as the test gasoline. The percentage content of isooctane in this blend is taken as numerically equal to the octane number of the test gasoline.

The octane numbers of automotive gasolines higher than 100 are determined by comparing a gasoline with isooctane to which an antiknock -- tetraethyl lead -- has been added.

The Motor and the Research methods of determining octane number are differentiated by the test procedures*:

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* The composition of the test mixture corresponds to the detonation maximum; a single-cylinder engine with a variable compression ratio (cylinder diameter 85 mm and piston stroke 115 mm) is used for experiments in both cases.

	Motor Method	Research Method
Stand for tests	IT 9-2	IT 9-6
n, rpm	900±10	600±6
Temperature, °C		
in the cooling system	100±2	100±2
air heating	40-50	52±1
mixture heating	149±1	Is not heated
heating of oil in crankcase	50-75	50-75
θ, °	26 ($\varepsilon = 5.0$) 19 ($\varepsilon = 7.0$)	13

Gasoline tests by the Research Method are conducted in a less intense engine operating regime than by the Motor Method. Therefore the octane number of gasoline determined by the Research Method is usually higher than the octane number determined by the Motor Method. The difference in octane numbers of gasoline found by these two methods is called gasoline sensitivity. Gasoline sensitivity is determined by its chemical composition.

A comparison of octane numbers with the behavior of gasolines in road conditions showed that the Research Method characterizes to some extent the antiknock properties of gasolines when an engine is operated under road traffic conditions with relatively low thermal stresses. When the thermal regime of an engine is intensified (prolonged suburban traffic, travel over poor roads, carrying of heavy loads, driving through passes, and so on), the behavior of a gasoline with respect to its knock resistance corresponds more closely to the octane number determined by the Motor Method.

The correspondence of gasoline octane numbers determined by either laboratory method to the actual knock resistance of the gasolines in road conditions depends not only on the design characteristics of the engine itself, but also on the type of transmission used in the given vehicle. In a motor vehicle with manual transmission engine operation with throttle wide open is possible at a relatively low rpm. The maximum knocking in this case is usually observed at low rpm settings and the Research Method of rating octane numbers more precisely reflects the behavior of a fuel in road conditions.

With automatic transmission, an engine cannot operate at low rpm with throttle wide open. Therefore, detonation commences in the high rpm range and the behavior of a gasoline in road conditions is more precisely rated by the Motor Method of determining octane numbers.

The different ratings of knock resistance of gasolines in laboratory and road conditions served as the basis for conducting a complex of studies on full-sized engines.

In 1932-1933 road tests of fuels on motor vehicles with the aim of developing a method for rating their antiknock properties in actual conditions and for comparing these data with laboratory findings were conducted for the first time in the United States, in Uniontown. The road test method at that time, referred as the Uniontown Method, or the knocking maximum method, consists of determining the highest rate of fuel knock with slow vehicular acceleration and seeking to find blends of reference fuels causing the same knocking rate, regardless of whether it occurs at any given velocity. The knocking rate was determined by listening, and the acceleration was carried out with throttle wide open in order to reduce the drag of the vehicle /1/. Later the Uniontown Method was supplemented by recording the knocking rate during acceleration and began to be called the modified Uniontown Method.

Due to shortcomings in the Uniontown Method, in 1940 broad comprehensive tests were made in the United States in the city of San Bernardino aimed at formulating a new method of road knock testing. This method, called the San Bernardino Method, or the Borderline Method, consists of determining the velocity at which knocking ends when a motor vehicle is accelerated at a minimum velocity with the throttle wide open on a road with constant grade. The bounding ignition advance was determined as a function of vehicular speed for test fuels and for reference fuels. To eliminate operating conditions with an increased knocking rate, subsequently continuous manual control of ignition advance during acceleration was used until the beginning of audible knocking, and the method then began to be called the modified Borderline Method /1/. In recent years American methods of knock testing have remained fundamentally unchanged and are used with minor improvements up to the present time.

In the USSR, a method of knock testing of full-sized automotive engines and gasolines was developed by D. M. Aronov and L. V. Malyavinskiy and was standardized in 1963 /16-19/. The method (GOST 10373-63) is intended for determining actual octane numbers of automotive gasolines and engine requirements for knock resistance of gasolines used. It found application in finishing studies involved in building new or modernizing existing engines, in determining their requirements for gasoline knock resistance, in rating actual antiknock properties of commercial and new grades of automotive fuels and their components, and also in studying engine working processes and the knock resistance of fuels. The method provides for knock tests of an engine (on a motor braking stand with standard equipment) or a vehicle.

Stand tests provide the knock characteristic of an engine over the entire range of rpm values and thus the knock characteristics of test gasolines, showing their actual antiknock properties for the given engine.

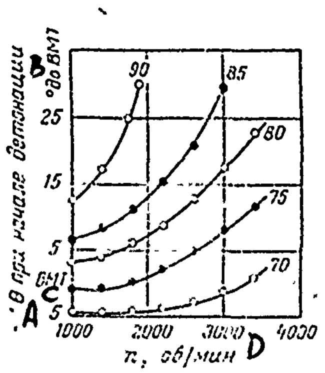

Fig. 32. Primary knock characteristic of an engine: the numbers alongside the lines are the octane numbers of a blend of reference fuels.
KEY: A -- θ at the outset of knocking
B -- ° before TDC
C -- TDC
D -- rpm

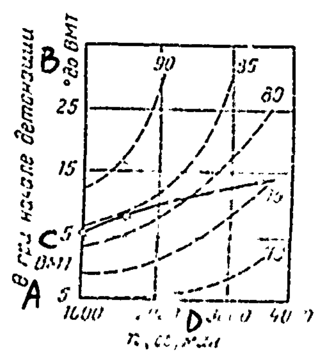

Fig. 33. Primary knock characteristic of gasoline (bold line)
KEY: A -- θ at the outset of knocking
B -- ° before TDC
C -- TDC
D -- rpm

The road test method is simplified compared with the stand test method. Here the antiknock properties of gasolines are rated not by the characteristic, but by the point.

Essentially, the knock test method reduces to the following. In the actual engine operating regime with which the most favorable conditions for the inception of knocking are produced (full load, normal thermal regime, and normal adjustment of mixture composition), a determination is made of the dependence of the ignition advance causing the onset of audible knocking on the engine rpm for a number of blends of reference fuels. The test results are depicted in the form of the primary knock characteristic of the test gasoline, which is then aligned with the primary knock characteristic of the engine (Fig. 33).

An intermediate knock characteristic (Fig. 34) in the following coordinates is plotted based on these data: octane numbers of blends of reference fuels versus the ignition advance for which the primary knock characteristic of the engine is intersected by several lines corresponding to constant rpm settings, and for each rpm the dependence of the ignition advance on the octane number of the blend of reference fuels is determined (Fig. 34). Data for the test gasoline taken from the composite graph (Fig. 33) are plotted on the same intermediate knock characteristic.

Using the intermediate knock characteristic, one constucts a summary curve in the following coordinates: actual octane number of the gasoline versus the engine crankshaft rpm (Fig. 35). By the actual octane number (AON) of a gasoline is meant the octane number determined by the Motor Method for a blend of reference fuels exhibiting knock resistance in test conditions that is the same as the knock resistance of the test gasoline.

This same procedure is used in rating the requirements of automotive engines for the knock resistance of gasolines and improvements in engine design, that is, the completeness of the use made of gasoline antiknock properties in a specific engine.

Advances and design improvements in automotive engines and the finding of characteristics of high-octane gasoline use necessitate seeking ways of improving and refining knock test procedures.

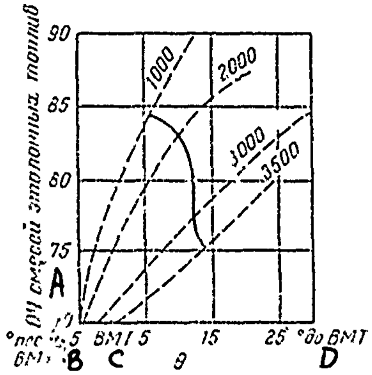

Fig. 34. Intermediate knock characteristic of a gasoline (bold line), the numbers by the lines stand for n.
KEY: A -- ON [octane number] of blends of reference fuels
B -- ° past TDC
C -- TDC
D -- ° before TDC

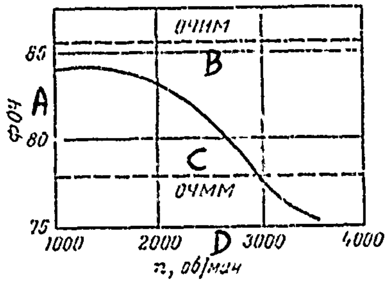

Fig. 35. Summary knock characteristic of a gasoline
KEY: A -- AON
B -- ONRM
C -- ONMM
D -- rpm

The widespread CFR test engine differs markedly from modern automotive engines in the shape and cooling conditions of the combustion chamber, and also in the velocity regime. A new single-cylinder engine, liquid-cooled with variable compression ratio, was developed and proposed for octane number rating [20, 21]. The shape of its combustion chamber, its cooling scheme, and the arrangement of valves and spark plug are approximately the same as in modern engines. The maximum rpm is 5000. Varying the compression ratio from 6.6 to 13.7 is achieved by rotating the circular supports bearing eccentrically positioned main bearings.

There are several modifications of intake systems simulating the separation of individual gasoline fractions (fractionation) in the intake manifold. In particular, a standard intake manifold was proposed for the standard CFR stand; a metal insert is positioned in the intake manifold in the direction of the flow of the mixture from carburetor to cylinder (Fig. 36). This section of the line is surrounded with a cooling sleeve so that part of the mixture condenses, the condensate is removed, and its amount is measured. The octane number thus obtained is called the "distribution octane number."

A method using racing drums was proposed for rating the knock resistance of fuels intended for trucks [25, 26]. So-called "knock maps" are compiled from the test results, and with these maps the actual knock resistance of gasolines is then determined [27-29].

An interesting idea is the multiregime laboratory method of octane number determination suggested by D. M. Aronov [1]. The multiregime method provides for determining the knock resistance of gasolines in several regimes using two pairs of reference fuels. One pair of reference fuels is virtually insensitive to the determination regime (isooctane-heptane), while the other pair is composed of sensitive fuels (diisobutylene or toluene and heptane). Determining the knock qualities of gasolines by the multiregime method evidently brings the laboratory rating closer to the actual behavior of gasolines in a full-sized engine.

At the same time with the development and improvement of motor methods of rating the knock resistance of gasoline, efforts to find a relationship between this indicator and gasoline properties easily determined in laboratory conditions are continuing.

It was proposed [30] to rate the octane number of a fuel on the basis of its dielectric permeability. The dielectric permeability E of hydrocarbons depends on their structure. It is higher for aromatic hydrocarbons than for paraffinic (data at 30° C):

Pentane	1.820	Benzene	2.266
Hexane	1.870	Toluene	2.360
Heptane	1.912	m-Xylene	2.370
Octane	1.935	o-Xylene	2.553
Nonane	1.935	p-Xylene	2.260
Decane	1.937		

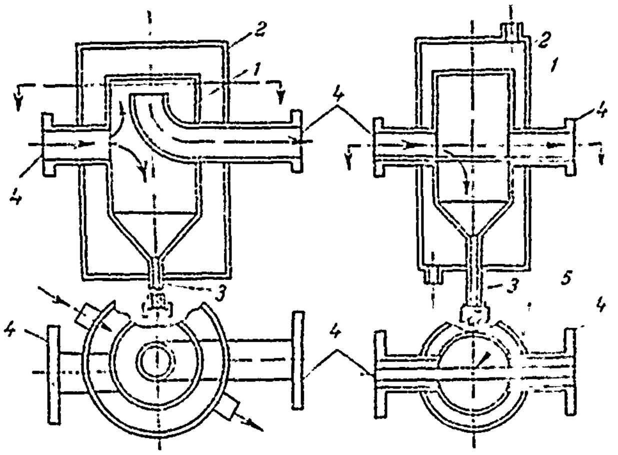

Fig. 36. Two designs for an insert to be placed in the intake manifold for determining octane numbers by the DON /distribution octane number/ method. The arrows indicate the flow direction of the combustible mixture:

1 -- expansion vessel
2 -- housing of water system for cooling the expansion vessel
3 -- condensate bleed valve
4 -- connecting flanges
5 -- groove for feeding liquid film into engine cylinder

On this basis, the author found a relationship between the dielectric permeability of gasoline and its octane number (Fig. 37). It was suggested to rate the octane number of gasoline with a special instrument by comparing the E values of the test fuel and a reference fuel /30/. Naturally, the precision of this method is not high.

It was proposed /31/ to determine the octane number of gasoline by using the known values of its gravity and the 10 percent and 90 percent distillation temperatures (t_{10} and t_{90}).

The following empirical formula is recommended for gasolines with octane numbers higher than 62:

$$\mathrm{ON} = 1020{,}7 - 64{,}86\left[4\lg\left(\frac{141{,}5}{\rho^{15}} - 131{,}5\right) + 2\lg\left(\frac{9}{5}t_{10} + 32\right) + 1{,}3\lg\left(\frac{9}{5}t_{90} + 32\right)\right]$$

More exact data on octane numbers can be obtained by using the following empirical formula /32/:

$$\text{ONMM} = 100 - \rho_4^{20} \frac{t_{e.b} + P}{C t_{e.b}} \cdot \frac{1}{A} + C - A$$

where P is the aniline point of the gasoline*, °C; C is the volatility coefficient of gasoline, equal to $\frac{t_{10} + t_{50} + t_{90}}{100}$; and A is the slope of the gasoline distillation curve, equal to $\frac{t_{90} - t_{10}}{80}$.

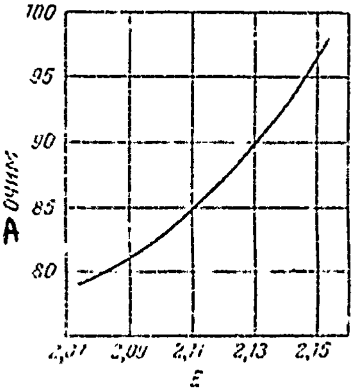

Fig. 37. Dependence of knock resistance of gasolines on their dielectric perrea- bility /30/
KEY: A — ONMM

The above-presented formula is suitable for gasolines in which the ratio $(t_{e.b}/t_{10}) \cdot A > 1.9$; if it is smaller than 1.9, then the formula given below must be used:

$$\text{ONMM} = 100 \frac{(t_{e.b} + P)\, t_{e.b}}{10 P \rho_4^{20} C \sqrt{t_{e.b}}} \left(\rho_4^{20} + \rho_4^{20} A + \frac{t_{e.b}}{10P} + \rho_4^{20} CA\right)$$

Both of the above-presented formulas are applicable to gasolines prepared by direct distillation, thermal cracking, and thermal reforming, as well as to all other gasolines for which the inequality $P < t_{10} < 2P$ is valid.

The following empirical formula

---

* The aniline point characterizes the chemical composition of gasoline.

$$\mathrm{ONMM} = 22.5 + 0.83\ \mathrm{ONRM} - 20\ \rho_{15}^{15} - 0.12\ C_1 + 2.3\ C_2 + 0.9\ C_3$$

where C_1, C_2, and C_3 represent the gasoline content of olefins (percent by volume), TML, and TEL, respectively, ml/l, was proposed [33] for the determination of octane numbers based on the Motor Method, via calculation (knowing the octane number based on the Research Method).

Engine Requirements on Gasoline Knock Resistance

The requirements of an automotive engine on the knock resistance of gasolines used, ON_f [f = fuel], are determined by the complex of its design characteristics, among which the compression ratio and the cylinder diameter are the most significant. The following empirical formula was derived relating these three indicators [1, 34, 35]:

$$\mathrm{ON}_f = 125{,}4 - \frac{413}{\varepsilon} + 0{,}183d$$

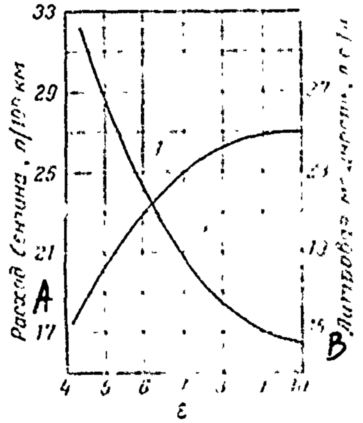

Fig. 38. Effect of compression ratio on fuel consumption and liter power output of engine:
1 -- liter power output, hp/l
2 -- fuel consumption, l/100 km
KEY: A -- Fuel consumption, l/100 km
B -- Liter power output, hp/l

Improvements in automotive engine building are bound up with the steady rise in the compression ratio. This trend is primary in upgrading the design of automotive gasoline engines, since it permits improving their engineering-economic and operating indicators. Raising the compression ratio simultaneously improves two fundamental indicators (Fig. 38) -- it increases the liter power output 1 and reduces gasoline consumption 2.

Table 16 presents data on improvements made in automotive engines at the Moscow Automotive Plant imeni Leninskiy Komsomol. The increase in the compression ratio was accompanied by improvement in power indicators, with a simultaneous rise in the requirements for the knock resistance of gasolines used.

Table 16. Improvements in the Moskvich automotive engines [1]

Марка двигателя 1	ε	Удельные мощностные показатели 2		ОЧММ рекомендуемого бензина 4
		$N^*_{ло}$ 3	$p^{**}_{e\,max}$	
«Москвич-400» 5	6,0	5,72	5,95	66
«Москвич-402» 6	6,7	6,55	7,45	72
«Москвич-407» 7	7,0	7,71	8,50	72
«Москвич-408» 8	7,5	8,57	9,32	76
«Москвич-412» 9	8,2	9,18	9,69	85***

* Liter-rpm power output, hp/l at 1000 rpm
** Greatest mean effective pressure, kg/cm^2
*** AI-93 gasoline

KEY:
1 -- Engine model
2 -- Specific power output indicators
3 -- N^*_{1-r}
4 -- ONMM of recommended gasoline
5 -- Moskvich-400
6 -- Moskvich-402
7 -- Moskvich-407
8 -- Moskvich-408
9 -- Moskvich-412

Thus, design advances and improvements in automotive engines are attended by intensified requirements on the knock resistance of gasolines used. Progress in petroleum refinery is also directed at improving the antiknock qualities of automotive gasolines. However, an increase in the octane numbers of gasolines produced involves the necessity of complicated and expensive processes and therefore, greater capital investments and higher costs for gasoline. Modern production processes aimed at boosting the knock resistance (reforming, isomerization, alkylation, and so on) are not accompanied by an increased yield of gasoline from petroleum and so outlays for these processes must be recouped by savings from using higher-octane gasolines in engines with higher compression ratios. Accordingly, ensuring the fullest and most efficient use of automotive gasolines with the maximum matching between engine requirements and the antiknock qualities of the gasolines used is a paramount national-economic task. To perform it necessitates, on the one hand, detailed study of engine requirements for gasoline knock resistance [36, 37], and measurements of these requirements in different service conditions, and on the other -- a knowledge of the actual knock resistance of gasolines in various service conditions.

Ensuring complete matching between engine requirements and the actual knock resistance of gasolines used has taken on vital importance in recent years owing to the use of high-octane gasolines since the cost of each octane point rises sharply with an increase in the total gasoline knock resistance.

Presently, in our country the automotive engine requirements on gasoline knock resistance are determined on the basis of GOST 10373-63, that is, the same standard with which the actual octane numbers of gasolines are determined. Essentially, the method consists of finding relationships between the power output or specific fuel consumption and the ignition advance for a series of high-speed regimes with full throttle. Ignition advance causing trace knock with blends of reference fuels with different octane numbers for operation at various rpm's is also determined. Test results are used to determine to antiknock requirements of an engine in different rpm settings corresponding to the octane number of a reference blend providing the highest power output and the lowest specific fuel consumption when the engine is run at trace knock /19/. Table 17 presents the results of determining the requirements imposed on domestic automotive engines for gasoline knock resistance.

These data show convincingly that the requirement for high-octane gasoline develops only for a restricted range of engine operating regimes. For the other regimes it is quite possible to use low-octane and therefore cheaper fuels. So a number of efforts were made to achieve separate feed of an engine in regimes of full and partial loads by using a dual feed system or by injection of antiknock or coolant additives in the full load regimes. These procedures failed to gain wide practical use owing to the sizable complexity of the feed systems and the loss in their reliability.

Efforts toward the fuller use of fuel knock resistance and improvement in fuel operating economy in engines in partial loads led to a number of designs for engines for variable compression ratios /38/. The proposed designs provide for boosting the engine compression ratio in partial load regimes when this is not limited by knock. Unfortunately, design complications introduced into variable compression-ratio engines are thus far so extensive that they are not compensated by the advantages gained.

When one examines the results of rating the antiknock requirements of engines (cf. Table 17), one can note that the octane numbers of recommended gasolines and gasolines actually used in engines are much lower than those required for several regimes. This is accounted for by the following factors. The highest antiknock qualities of a gasoline are required by an engine when it is operating in several regimes with 100 percent power output. It was noted that whereas in these regimes the ignition advance must be shifted somewhat compared with the optimal values, the antiknock requirements of an engine decrease quite abruptly for a relatively small drop in the power-output indicators. As a result of tests, it was found that adjustment of late ignition advance causing a decrease in power by more than 5 percent leads to an interruption in the exhaust system and a reduction in engine operating stability, therefore the 5 percent power loss can be taken as an estimate in determining the allowable reduction in engine antiknock requirements. The gasoline octane numbers obtained in this manner required for the operation of an engine with a 5 percent power loss can be provisionally called the minimum allowable value. Ignition advance automatic devices are adjusted at the plant so as to ensure the use of gasolines with the minimum allowable octane numbers.

Table 17. Requirements of domestic automotive engines on gasoline knock resistance [1]

n, об/мин 1	Показатель 2	ЗАЗ-966 3	«Москвич-408» 4	ГАЗ-21 5	ГАЗ-53 6	ЗИЛ-130 7	ЗИЛ-375 8
1000	θ °ПКВ 9	24	30	30	30	34	32
	ОЧ$_{\text{Т}}$ 10	87,0	83,0	82,0	80,0	86,0	82,0
1500	θ °ПКВ 9	26	34	33	35	36	34
	ОЧ$_{\text{Т}}$ 10	85,0	82,0	79,0	80,0	82,5	79,0
2000	θ °ПКВ 9	29	38	35	38	38	36
	ОЧ$_{\text{Т}}$ 10	82,5	81,0	75,5	75,0	78,5	76,0
2500	θ °ПКВ 9	32	41	37	41	39	38
	ОЧ$_{\text{Т}}$ 10	80,0	80,0	71,0	73,0	73,5	72,0
3000	θ °ПКВ 9	37	44	41	46	41	39
	ОЧ$_{\text{Т}}$ 10	77,0	79,0	65,0	69,0	68,5	68,5
3500	θ °ПКВ 9	42	47	45	—	—	—
	ОЧ$_{\text{Т}}$ 10	74,0	75,5	59,0	—	—	—
4000	θ °ПКВ 9	44	48	51	—	—	—
	ОЧ$_{\text{Т}}$ 10	70,5	71,0	52,0	—	—	—

KEY: 1 -- n, rpm
2 -- Indicator
3 -- ZAZ-966
4 -- Moskvich-408
5 -- GAZ-21
6 -- GAZ-53
7 -- ZIL-130
8 -- ZIL-375
9 -- ° Crank angle
10 -- ON$_f$

D. M. Aronov [1] made a determination of the minimum allowable octane numbers for a series of domestic engines (Table 18) and found a dependence of the allowable decrease in octane numbers ΔON on the level of the initial requirements ON$_f$:

$$\Delta \text{ON} = 45.6 - 0.415\,(\text{ON}_f)\quad .$$

This function shows that the allowance decrease in octane numbers due to adjustment of a latter ignition advance becomes smaller when the initial requirements are raised. In other words, as the total level of antiknock requirements goes up (cf. Table 18), allowance deviations in the octane numbers of fuels used decrease. This highly central factor must be borne in mind when designing new engines.

Table 18. Decrease in antiknock requirements on fuel when there is a 5 percent degradation in engine operating indicators /1/

Двигатель 1	ОЧ$_г$ 2	ΔОЧ 3	Минимально допустимые ОЧ 4
ГАЗ-20, ГАЗ-51, ЗИЛ-164 5	70—78	15	55—63
ГАЗ-21, «Москвич-407» 6	82—84	12	70—72
ЗАЗ-966, ЗИЛ-130 7	86—87	10	76—77

KEY: 1 -- Engine
2 -- ON_f
3 -- ΔON
4 -- Maximum allowance ON
5 -- GAZ-20, GAZ-51, and ZIL-164
6 -- GAZ-21, Moskvich-407
7 -- ZAZ-966 and ZIL-130

Engine requirements are determined by using primary reference fuels -- blends of isooctane and heptane. The octane number of such a blend is determined by the isooctane content and does not depend on the test conditions and the engine operating regime. However, a study of the antiknock properties of automotive gasolines on single-cylinder installations and full-sized engines in various operating regimes showed that gasolines differing in hydrocarbon content respond differently to changes in test regimes and thus their antiknock properties depend on the engine operating regime. It was already noted earlier that the octane numbers of gasolines determined in various regimes (Research and Motor methods) can differ by 10-15 points, that is, the gasolines exhibit different "sensitivity" to engine operating regimes. The difference between octane numbers determined by the Research and Motor methods is used for the quantitative estimate of fuel sensitivity.

When a sensitive gasoline is used in an engine, its actual knock resistance can be closer to the octane number determined by the Research Method or the octane number found by the Motor Method. The nature of the gasoline rating in this case depends on the severity of the engine operating regime.

Regime severity refers to not some one parameter, but an array of parameters influencing the rating of antiknock properties /39/.

Conventionally, the knock severity of an automotive engine expressed in terms of the knock severity of the operating regime according to the Research or the Motor methods has been proposed for a quantitative estimate /39/. The knock severity of an engine for a given regime Zh is determined by the formula

$$Zh = \frac{ONRM - AON}{ONRM - ONMM} \cdot 10 ,$$

where ONRM, ONMM, and AON are the corresponding octane characteristics of the sensitive fuel.

The knock severity of the Motor Method is conventionally expressed as 10 points, and the knock severity of the Research Method is taken as 0. Thus, in an engine with a knock severity of 10, actual octane numbers of gasolines will be equal to ONMM, and for a severity of 0 they will be equal to ONRM. If the engine regime severity is more than 10, the actual octane numbers of the gasolines will be smaller for this regime than their ONMM, but if the severity is smaller than 0, the actual octane numbers will be larger than their ONRM.

For a full characterization of an engine, its knock severity is determined for several optimal operating regimes using sensitive reference fuels (blends of diisobutylene with n-heptane). Fig. 39 shows the results of a determination of knock severity for a series of domestic engines of passenger cars and trucks.

Investigations showed that as the rpm is increased, engine severity rises (Fig. 40). A rise in the compression ratio causes a reduction in severity, while a rise in the air temperature leads to its slight rise /39/.

Knock severity is a vital criterion for evaluating the perfection of automotive engine design, since engines with low severity can make better use of the antiknock properties of sensitive fuels. It must be borne in mind that most modern and prospective automotive gasolines have fairly high sensitivities, amounting to as much as 10-12 points.

It has been proposed /1, 19/ to use two additional dimensionless criteria -- the knock index and the index of engine use of fuel knock resistance, KT and KRU /respectively/ -- in evaluating perfection of engines as to their antiknock requirements. These indicators make possible a comparison of the results of knock tests of a given engine with mean-statistical data for engines of the same size. Knock index refers to the following ratio:

$$KI = \frac{ON_f^c}{ON_f^a},$$

where ON_f^c is the required octane number determined by calculation based on the compression ratio and cylinder diameter; ON_f^a is the actually required octane number based on results of knock tests made on the given engine.

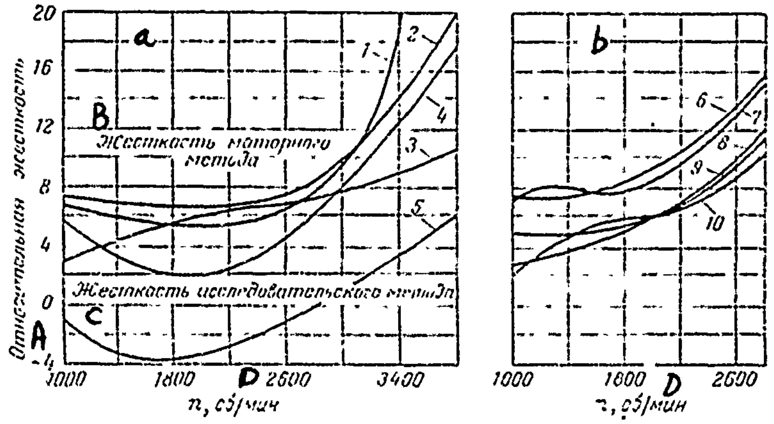

Fig. 39. Characteristics of engine knock severity:
a -- passenger cars b -- trucks /39/
1 -- Volga M-21 6 -- ZIL-130
2 -- ZAZ-966 7 -- ZIL-375
3 -- Moskvich-408 8 -- Ural-376
4 -- Moskvich-407 9 -- Ural-378
5 -- Moskvich-401M 10 -- Ural-374
KEY: A -- Relative severity
B -- Severity of Motor Method
C -- Severity of Research Method
D -- rpm

The knock index permits engines to be compared by their requirements on gasoline knock resistance, however a reduction in the required octane numbers can be achieved also by a deterioration in the operating engine indicators. The index of knock resistance use KRU serves as an evaluation of engine design for these purposes:

$$KRU_N = \frac{N_{l.r}^{ac}}{N_{l.r}^{cal}},$$

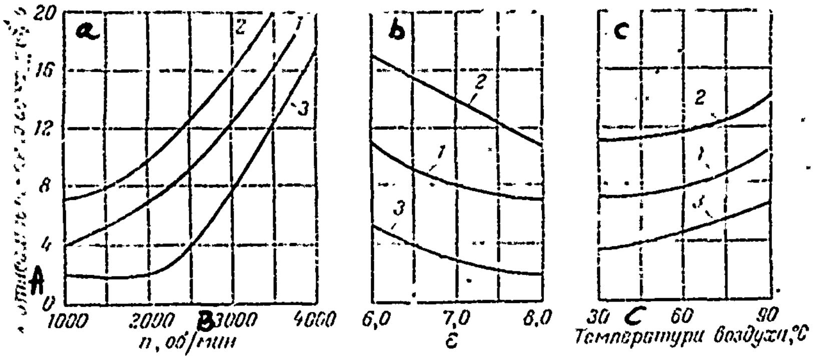

Fig. 40. Dependence of knock severity of engine on crankshaft rpm (a), compression ratio (b), and air temperature (c) /39/:
1, 2, 3 -- mean, maximum, and minimum knock severity of engine
KEY: A -- Relative severity
B -- rpm
C -- Air temperature

$$KRU_{cal} = \frac{P_e^{ac}}{P_c^{cal}},$$

where $N_{l.r}^{ac}$ and P_e^{ac} are the actual maximum liter-rpm power and mean effective pressure values, determined in tests; $N_{l.r}^{ac}$ and P_e^{ac} are the same quantities, determined by calculation based on the known actual antiknock requirements.

Thus, the knock index of an engine shows by how much its antiknock requirements differ from the mean requirements for similar engines. The knock resistance use index shows by how much a fuel is used better or more poorly in a given engine than in the average engine. From the determination it follows that the engines which have knock indexes and knock resistance index uses greater than unity are better and more advanced engines.

Table 19. Values of dimensionless criteria of the perfection of domestic automotive engines [1]

Марка двигателя 1	ДП 2	ИДС$_N$ 3	.ИДС$_р$ 4
МеМз-966 5	0,864	0,954	0,876
«Москвич-407» 6	0,975	1,100	1,011
«Москвич-408» 7	0,979	1,071	1,040
«Москвич-412» 8	0,970	1,000	0,960
ГАЗ-21 9	1,001	0,963	1,007
ГАЗ-24 10	1,022	0,930	1,020
ЗИЛ-130 11	0,984	0,974	0,887
ЗИЛ-375 12	0,996	0,970	0,957
ГАЗ-53 13	0,990	1,080	1,071
«Урал-374» 14	0,974	1,013	1,001
«Урал-376» 15	0,996	0,997	0,980

KEY: 1 -- Engine model
2 -- KI
3 -- KRU_N
4 -- KRU_{cal}
5 -- MeMz-966
6 -- Moskvich-407
7 -- Moskvich-408
8 -- Moskvich-412
9 -- GAZ-21
10 -- GAZ-24
11 -- ZIL-130
12 -- ZIL-375
13 -- GAZ-53
14 -- Ural-374
15 -- Ural-376

Table 19 presents the results of rating the technical advancement in several domestic automotive engines based on the above-presented dimensionless indicators.

Automotive engine requirements on the knock resistance of gasolines, set in stand conditions, can differ widely under the effect of various regime parameters and operating conditions. Fig. 41 presents several plots showing the dependence of their requirements imposed on gasoline octane numbers on change in certain engine regime parameters [40]. Fig. 41 a shows the effect on knock requirements imposed on fuel of the rpm with throttle wide open, power tuning of carburetor, and optimal ignition advance. The largest knock requirements in the given case corresponds to the smallest rpm. However, the ON_f maximum sometimes lies in the range of high rpm values, close to the rpm corresponding to the maximum torque. With an increase or decrease in the rpm with respect to this point, the knock requirements become less.

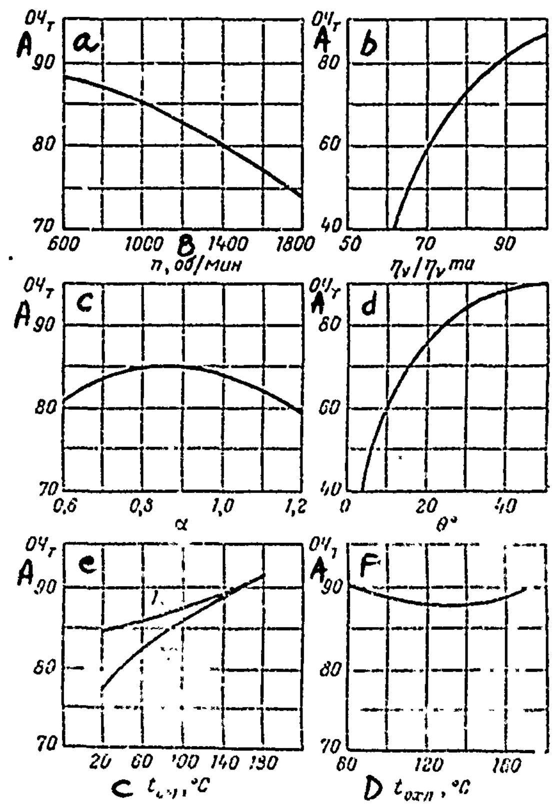

Fig. 41. Effect of main engine regime parameters on gasoline ON requirements /40/ ($\eta_V/\eta_{V_{max}}$ is the extent of engine throttling at constant rpm;

t_m is the mixture temperature, °C

t_{co} is the temperature of the coolant, °C)

1 -- with fully open throttle

2 -- with alternating open of throttle, which corresponds to constant charging

KEY: A -- ON_f

B -- rpm

C -- t_m

D -- t_{co}

Fig. 41 b shows the dependence of ON_f on load (throttling) of an engine at constant rpm, constant carburetor power tuning, and optimal ignition advance. The maximum ON_f values correspond to full throttle openings; these requirements fall off rapidly with increasing engine throttling.

Fig. 41 c shows the dependence of ON_f on the mixture composition with total throttle opening, constant rpm, and optimal ignition advance. The largest ON_f values observed for a mixture composition cause to power tuning.

Fig. 41 d shows the effect of the ignition advance on ON_f for total throttle opening, constant rpm, and carburetor power tuning. The ON_f values in this case increase with the ignition advance; however, gradually this rise slows down. It must be noted that ON_f values continue to increase even after a rise in the ignition advance angle above the optimal value when the engine indicators begin to deteriorate [40].

Fig. 41 e shows the effect of the mixture temperature on ON_f at constant rpm, carburetor power tuning, and optimal ignition advance for two cases of charging: 1 -- with throttle wide open and 2 -- for alternating opening of throttle corresponding to constant charging, equal to charging at highest mixture temperature. From the plot we see that with constant throttle opening, just as at constant filling a rise in the mixture temperature raises the required octane number.

Fig. 41 f illustrates the effect of the cooling temperature on the required octane number. In this case variation in the cooling temperature had a small effect on the required octane number.

All the experimental data presented in Fig. 41 were obtained on the same engine. Investigation of several other engines showed that the functions are common to all carburetor engines in their trend [40], however the quantitative effect of particular parameters can differ widely from the above-presented values. For example, requirements of the single-cylinder engine in the IT-9 stand, with variation in cooling temperature from 100 to 120° C, increased by 2.0 points, and for a 100 to 140° C temperature rise -- by 9.2 units, which considerably exceeds the value shown in Fig. 41 [41].

The engine requirements on fuel knock resistance established on the stand can vary widely under operating conditions.

The antiknock requirements of an engine climb when carbon deposits are formed in the combustion chambers and scale in the cooling system. The rise in the requirements is associated mainly with deterioration and heat removal. Studies showed that the antiknock requirements of an automotive engine during its operating time rise by an average of 4-6 points, and in some engines -- by 10-15 points. The different requirements occur uniformly

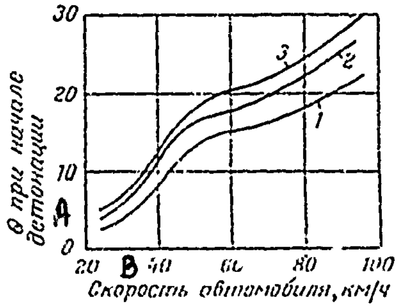

Fig. 42. Effect of carbon and scale deposits on the knock characteristic of an engine [1]:

1 -- after a run of 6000 km
2 -- after removal of carbon deposits
3 -- after removal of carbon and scale deposits
KEY: A -- θ at the outset of knocking
B -- Vehicle speed, km/hr

in the initial period of vehicular operation and becomes stabilized after 10,000 - 15,000 km. Cleaning engine free of deposits and scale reduces the ON_r (Fig. 42).

The antiknock requirements of an engine depend also on the climatic conditions of service. The cooling air temperature directly affects the mixture temperature and the cooling temperature, that is, the parameters whose effect on engine requirements we examined earlier (Fig. 41). A rise in humidity and the reduction in atmospheric pressure lead to a reduction in the requirements on fuel knock resistance.

Investigations showed [41] that for the normal operation of automotive engines in areas of dry hot climate, fuels with knock resistance approximately 6-8 octane points higher than the requirements for the given engine in ordinary conditions are required. In areas with humid tropical climate, the increase in requirements caused by the higher air temperature are practically entirely compensated by the reduction in the requirements owing to the higher humidity.

It must be noted that the necessity of using higher-octane gasolines is dictated not only by the rise in the antiknock requirements of a gasoline when certain operating conditions are varied, but also by the reduction in the actual octane number of gasolines exhibiting positive sensitivity. These characteristics of automotive gasoline use will be discussed in the next section.

Table 20. Antiknock properties of hydrocarbons [15]

Углеводороды 1	ОЧИМ 2	ОЧММ 3	Ч 4
Парафиновые 5			
н-Бутан 6	93,6	91,0	+2,6
Изобутан 7	101,1	99,0	+2,1
н-Пентан 8	61,7	61,9	−0,2
Изопентан (2-метилбутан) 9	92,3	90,3	+2,0
2,2-Диметилпропан 10	85,5	83,0	+2,5
н-Гексан 11	24,8	26,0	−1,2
2-Метилпентан 12	73,4	73,5	0,1
3-Метилпентан 13	74,3	74,5	+0,2
2,2-Диметилбутан (неогексан) 14	91,8	93,4	−1,6
2,3-Диметилбутан (диизопропил) 15	101,7	94,3	+7,4
н-Гептан 16	0	0	0
2-Метилгексан 17	42,4	46,4	−1,0
3-Метилгексан 18	52,0	55,0	−3,0
2,2-Диметилпентан 19	92,8	95,6	−2,8
2,3-Диметилпентан 20	91,1	88,5	+1,6
2,4-Диметилпентан 21	83,1	83,8	−0,7
3,3-Диметилпентан 22	80,8	86,6	−5,8
3-Этилпентан 23	65,0	69,3	−4,3
2,2,3-Триметилбутан (триптан) 24	105,7	101,0	+4,7
н-Октан 25	<0	−28	—
2-Метилгептан 26	21,7	23,8	−2,1
3-Метилгептан 27	26,8	35,0	−8,2
4-Метилгептан 28	26,7	38,0	−11,3
3-Этилгексан 29	33,5	52,4	−18,9
2,2-Диметилгексан 30	72,5	77,4	−4,9
2,3-Диметилгексан 31	71,3	78,9	−7,6
2,4-Диметилгексан 32	65,2	69,9	−4,7
2,5-Диметилгексан 33	55,5	55,7	−0,2
3,3-Диметилгексан 34	75,5	83,4	−7,9
3,4-Диметилгексан 35	76,3	81,7	−5,4
2-Метил-3-этилпентан 36	87,3	88,1	−0,8
3-Метил-3-этилпентан 37	80,8	88,7	−7,9
2,2,3-Триметилпентан 38	101,5	102,0	+2,5
2,2,4-Триметилпентан (изооктан) 39	100,0	100,0	0
2,3,3-Триметилпентан 40	102,9	99,4	+3,5
2,3,4-Триметилпентан 41	101,3	95,9	+5,4
2,2,3,3-Тетраметилбутан 42	106,9	103,0	+3,9
Олефиновые 43			
Бутен-1 44	97,4	81,7	+15,7
Бутен-2 45	99,6	86,5	+13,1
Пентен-1 46	90,9	77,1	+13,8
2-Метилбутен-1 47	101,3	81,9	+19,4
2-Метилбутен-2 48	97,3	84,7	+12,6
Гексен-1 49	76,4	63,4	+13,0
Гексен-2 50	92,7	80,8	+11,9
Гексен-3 51	94,0	80,1	+13,9
2-Метилпентен-2 52	97,8	83,0	+14,8
2-Метилпентен-3 53	99,3	81,3	+15,0
2,2,4-Триметилпентен-3 54	101,7	86,2	+15,5
2,2,4-Триметилпентен-4 55	102,9	88,6	+14,3
Нафтеновые 56			
Метилциклопентан 57	91,3	80,0	+11,3
Этилциклопентан 58	67,2	61,2	+6,0
н-Пропилциклопентан 59	31,2	28,1	+3,1
Изобутилциклопентан 60	33,4	28,2	+5,2
Циклогексан 61	83,0	77,2	+5,8
Метилциклогексан 62	74,8	71,1	+3,7
Этилциклогексан 63	46,5	40,8	+5,7
1,2-Диметилциклогексан 64	80,9	78,6	+2,3
1,3-Диметилциклогексан 65	69,3	61,2	+5,1
1,1-Диметилциклогексан 66	67,8	62,2	+5,6
н-Пропилциклогексан 67	17,8	14,0	+3,8
Изопропилциклогексан 68	62,8	61,1	+1,7
Ароматические 69			
Бензол 70	113,0	111,6	+1,4
Толуол 71	115,7	102,1	+13,6
Этилбензол 72	106,0	97,9	+8,1
н-Пропилбензол 73	105,1	98,7	+6,4
Изопропилбензол (кумол) 74	110,0	99,3	+10,7
1-Метил-3-этилбензол 75	109,0	100,0	+9,0

/KEY to Table 20 on preceding page/:

1 -- Hydrocarbons
2 -- ONRM
3 -- ONMM
4 -- Sensitivity
5 -- Paraffinic
6 -- n-Butane
7 -- Isobutane
8 -- n-Pentane
9 -- Isopentane (2-methylbutane)
10 -- 2,2-Dimethylpropane
11 -- n-Hexane
12 -- 2-Methylpentane
13 -- 3-Methylpentane
14 -- 2,2-Dimethylbutane (neohexane)
15 -- 2,3-Dimethylbutane (diisopropyl)
16 -- n-Heptane
17 -- 2-Methylhexane
18 -- 3-Methylhexane
19 -- 2,2-Dimethylpentane
20 -- 2,3-Dimethylpentane
21 -- 2,4-Dimethylpentane
22 -- 3,3-Dimethylpentane
23 -- 3-Ethylpentane
24 -- 2,2,3-Trimethylbutane (triptane)
25 -- n-Octane
26 -- 2-Methylheptane
27 -- 3-Methylheptane
28 -- 4-Methylheptane
29 -- 3-Ethylhexane
30 -- 2,2-Dimethylhexane
31 -- 2,3-Dimethylhexane
32 -- 2,4-Dimethylhexane
33 -- 2,5-Dimethylhexane
34 -- 3,3-Dimethylhexane
35 -- 3,4-Dimethylhexane
36 -- 2-Methyl-3-ethylpentane
37 -- 3-Methyl-3-ethylpentane
38 -- 2,2,3-Trimethylpentane
39 -- 2,2,4-Trimethylpentane (isooctane)
40 -- 2,3,3-Trimethylpentane
41 -- 2,3,4-Trimethylpentane
42 -- 2,2,3,3-Tetramethylbutane
43 -- Olefinic
44 -- Butene-1
45 -- Butene-2
46 -- Pentene-1
47 -- 2-Methylbutene-1
48 -- 2-Methylbutene-2
49 -- Hexene-1
50 -- Hexene-2
51 -- Hexene-3
52 -- 2-Methylpentene-2
53 -- 2-Methylpentene-3
54 -- 2,2,4-Trimethylpentene-3
55 -- 2,2,4-Trimethylpentene-4
56 -- Naphthenic
57 -- Methylcyclopentane
58 -- Ethylcyclopentane
59 -- n-Propylcyclopentane
60 -- Isobutylcyclopentane
61 -- Cyclohexane
62 -- Methylcyclohexane
63 -- Ethylcyclohexane
64 -- 1,2-Dimethylcyclohexane
65 -- 1,3-Dimethylcyclohexane
66 -- 1,4-Dimethylcyclohexane
67 -- n-Propylcyclohexane
68 -- Isopropylcyclohexane
69 -- Aromatic
70 -- Benzene
71 -- Toluene
72 -- Ethylbenzene
73 -- n-Propylbenzene
74 -- Isopropylbenzene (cumene)
75 -- 1-Methyl-3-ethylbenzene

Antiknock Properties of Gasolines and Their Components

The relationship between structure of hydrocarbons and their antiknock properties has long since been established. In 1921 Ricardo determined the toluene numbers for 13 individual hydrocarbons and observed several correlations in the effect of hydrocarbon chemical structure on hydrocarbon knock resistance. In 1934 data were published dealing with the antiknock properties of 171 individual hydrocarbons, and in 1938 the knock resistance of 325 hydrocarbons of various structural types was determined in the American Petroleum Institute [1]. The experimental materials accumulated thus far (Table 20) reveal several correlations.

Of all the hydrocarbon classes represented in automotive gasolines, normal paraffinic hydrocarbons have the lowest knock resistance. Their knock resistance deteriorates with increase in the number of carbon atoms in the chain of normal paraffinic hydrocarbons. The transition from normal to isomeric structure is always accompanied by an improvement in the antiknock properties of paraffinic hydrocarbons. But even for isomeric paraffins, the relationship persists: with increase in the number of carbon atoms in the straight chain of an isoparaffinic hydrocarbon molecule, its knock resistance decreases. An increase in the branching of a molecule, the compact and symmetrical arrangement of methyl groups, and their increasing proximity to the molecule's center promote a rise in the knock resistance of isoparaffinic hydrocarbons.

Olefinic hydrocarbons have higher antiknock properties than normal paraffin hydrocarbons with the same number of carbon atoms. The effect of the structure of olefinic hydrocarbons on their knock resistance obeys roughly the same correlations as for paraffinic hydrocarbons. The knock resistance of olefins increases with decrease in chain length, increase in branching, and greater compactness of the molecule. The best antiknock properties are found for those olefins in which the double bond is closer to the center of the carbon chain. Among dienic hydrocarbons, those with conjugated arrangement of double bonds have higher knock resistance.

The knock resistance of naphthenic hydrocarbons is higher than for normal paraffinic hydrocarbons, but is lower than for aromatic hydrocarbons with the same number of carbon atoms in the molecule. A decrease in the length of side chains and greater side chain branching and compactness lead to an improvement in the antiknock properties of naphthenic hydrocarbons. True, the effect of these factors in naphthenic hydrocarbons is less marked compared with paraffinic and olefinic hydrocarbons.

Aromatic hydrocarbons exhibit high knock resistance. In contrast to other hydrocarbon classes, their knock resistance does not change with increase in the number of carbon atoms in the molecule; in contrast, a reduction in the length of the side chain and an increase in side chain branching improve the knock resistance of aromatic hydrocarbons. The same effect is achieved by the appearance in side chains of double bonds and the symmetrical arrangement of alkyl groups.

Above it was already pointed out that the difference between octane numbers of hydrocarbons determined by the research and the motor methods characterizes their sensitivity to the engine operating regime. Unsaturated hydrocarbons exhibit the highest sensitivity, and paraffinic hydrocarbons -- the lowest. A rise in engine temperature regime causes a decrease in the knock resistance of nearly all hydrocarbons. Paraffinic hydrocarbons are most sensitive to temperature change.

The effect of change in the crankshaft rpm on the knock resistance of hydrocarbons depends on the engine temperature conditions, the hydrocarbon class, and the knock resistance of the hydrocarbons. With an increase in rpm, the knock resistance of low-octane paraffins rises, while the low-octane naphthenes and olefins show a decrease in knock resistance. As the temperature increases, the effect of variation in crankshaft rpm becomes less.

Low-octane paraffinic hydrocarbons generally exhibit negative sensitivity, and high-octane paraffinic hydrocarbons show a positive sensitivity. For octanes with a single side methyl group, the negative sensitivity increases in absolute value as this group shifts closer to the center of the chain; two methyl groups are present, the analogous effect is observed with their increase in mutual proximity. In more complicated isomers of octane, no definite correlation has been detected between sensitivity and structure [42].

High-octane mono-olefinic hydrocarbons show very high sensitivity. As in the case of paraffins, the sensitivity of mono-olefins decreases with decrease in the octane numbers and becomes negative. Dienes exhibit an inverse dependence of sensitivity on knock resistance. The sensitivity of some of them amounts to 35-40 points and exceeds the value of this indicator for all other hydrocarbons.

The sensitivity of aromatic hydrocarbons is somewhat less than for olefins. Since a limited group of aromatic hydrocarbons is used in automotive gasolines, their sensitivity can be regarded as roughly constant and equal to 10-15 points.

Naphthenic hydrocarbons exhibit moderate sensitivity. Increasing the length of the side chain somewhat reduces the sensitivity. Branching of the side chain has only slight effect on sensitivity [42].

The antiknock properties of automotive gasolines and their components are practically entirely due to the content and structure of the constituent hydrocarbons. Nonhydrocarbon impurities have virtually no effect on fuel knock resistance. One must note only the decrease in the knock resistance of ethyl gasolines in the presence of organic sulfur compounds.

Table 21. Antiknock properties of straight-run gasolines from various crudes /15, 19/

Бензин (или фракция) 1	ОЧИМ 2	ОЧММ 3	Ч 4
Бензин н. к. —200° С (туймазинская нефть, Башкирия) 5	43,0	41,0	+2,0
Бензин н. к. —200° С (краснокамская нефть) 6	50,0	18,6	+1,4
Бензин н. к. —200° С (катанглийская нефть, о. Сахалин) 7	70,5	68,5	+2,5
Бензин н. к. —200° С (мухановская нефть, Куйбышевская обл.) 8	33,0	32,8	+0,2
Бензин н. к. —200° С (урицкая нефть, Саратовская обл.) 9	63,8	62,0	+1,8
Бензин н. к. —200° С (ромашкинская нефть, Татария) 10	41,6	41,0	+0,6
Фракция (н. к. —180° С) бензина прямой перегонки (ромашкинская нефть, Татария) 11	46,0	46,0	0,0
Фракция (н. к. —120° С) бензина прямой перегонки (ромашкинская нефть, Татария) 12	57,5	58,0	−0,5
Фракция (н. к. —85° С) бензина прямой перегонки (ромашкинская нефть, Татария) 13	67,0	68,0	−1,0
Фракция (н. к. —62° С) бензина прямой перегонки (ромашкинская нефть, Татария) 14	76,0	75,0	+1,0
Фракция (н. к. —62° С) бензина прямой перегонки (смесь нефтей Куйбышевской обл.) 15	75,0	73,2	+1,8

KEY: 1 -- Gasoline (or fraction)
2 -- ONRM
3 -- ONMM
4 -- Sensitivity
5 -- Gasoline, in. boil. -200° C (Tuymazy crude, Bashkiria)
6 -- Gasoline, in. boil. -200° C (Krasnokama crude)
7 -- Gasoline, in. boil. -200° C (Katangli crude, Sakhalin Island)
8 -- Gasoline, in. boil. -200° C (Mukhanovo crude, Kuybyshevskaya Oblast)
9 -- Gasoline, in. boil. -200° C (Uritskaya crude, Saratovskaya Oblast)
10 -- Gasoline, in. boil. -200° C (Romashkinskaya crude, Tataria)
11 -- Fraction (in. boil. -180° C) of straight-run gasoline (Romashkinskaya crude, Tataria)
12 -- Fraction (in. boil. -120° C) of straight-run gasoline (Romashkinskaya crude, Tataria)
13 -- Fraction (in. boil. -85° C) of straight-run gasoline (Romashkinskaya crude, Tataria)
14 -- Fraction (in. boil. -62° C) of straight-run gasoline (Romashkinskaya crude, Tataria)
15 -- Fraction (in. boil. -62° C) of straight-run gasoline (blend of Kuybyshevskaya Oblast crudes)

Table 22. Antiknock properties of thermal-process gasolines /15, 43, 44/

Бензин 1	ОЧИМ 2	ОЧММ 3	Ч 4
Бензин термического крекинга мазута 5			
из куйбышевских нефтей 6	71,2	64,2	7,0
из саратовских нефтей 7	73,4	66,4	7,0
Бензин термоконтактного крекинга гудрона арланской нефти 8	83,8	71,0	12,8
Он же после облагораживания 9	72,0	67,0	5,0
Бензин замедленного коксования гудрона 10	68,2	62,4	5,8
Бензин пиролиза этиленового режима после облагораживания 11	99,0	86,0	13,0
Бензин пиролиза бутиленового режима после облагораживания 12	74,3	68,8	5,5
Бензин термического крекинга полугудрона 13	75,6	68,5	7,1
Бензин с комбинированной установки термического крекинга мазута и термического риформинга лигроина 14	78,0	71,5	6,5
Бензин термического риформинга фракции 100—260° С на комбинированной установке 15	76,0	71,0	5,0

KEY: 1 -- Gasoline
2 -- ONRM
3 -- ONMM
4 -- Sensitivity
5 -- Gasoline from thermally cracked mazut
6 -- prepared from Kuybyshev crudes
7 -- prepared from Saratov crudes
8 -- Gasoline from thermocontact cracking of Arlanskaya crude
9 -- As above, after refinement
10 -- Gasoline from slow coking of gudron
11 -- Gasoline prepared by ethylene regime pyrolysis, after refining
12 -- Gasoline prepared by butylene regime pyrolysis, after refining
13 -- Gasoline prepared by thermal cracking of semigudron
14 -- Gasoline from combination unit for thermal cracking of mazut and thermal reforming of ligroin
15 -- Gasoline from the thermal reforming of the 100-260° C fraction on a combination unit

Modern commercial automotive gasolines as a rule are prepared by blending components obtained by direct distillation, thermal cracking, thermal reforming, catalytic cracking and catalytic reforming, coking, hydrocracking, alkylation, polymerization, isomerization, and other processes of refining petroleum and petroleum fractions. One of the decisive indicators governing the ratio of components in commercial gasolines is their knock resistance.

Straight-run gasolines as a rule contain a high paraffinic hydrocarbon content with weakly branched structure and low knock resistance. Their octane numbers are low (Table 21). Straight-run gasolines from sulfur crudes with 180-200° C end boiling points contain 60-80 percent paraffinic hydrocarbons and have octane numbers in the range 40-50. Straight-run gasolines with octane number at about 70 can be produced only from individual "select" crudes. However, the reserves of these crudes are very limited, and their refining at refineries, separately from other crudes, involves certain difficulties. Accordingly, at the present time even an aviation gasoline such as B-70 is prepared not by the direct distillation of special crudes, as was earlier, but by adding high-octane components to low-octane straight-run gasolines produced from ordinary crudes.

Straight-run gasolines thus far still remain the main component in the compounding of A-66 commercial gasolines; they are used in small amounts also in compounding A-72 and A-76 gasolines. Straight-run components are used to a very limited extent in higher-octane gasolines. Straight-run gasolines serve as feed for catalytic reforming units and other petrochemical facilities.

A reduction in the end boiling point of straight-run gasolines leads to a rise in their knock resistance. The -62° C initial boiling point fraction and the -85° C initial boiling point fraction of low-octane straight-run gasolines have octane numbers of 75 and 68, respectively, are used as automotive gasoline components.

Thermal cracking gasolines incorporate a high content of unsaturated hydrocarbons, whose knock resistance is higher than normal paraffins, therefore thermal cracking gasolines usually have higher octane numbers than straight-run gasolines refined from the same crudes (Table 22). Octane numbers of thermal cracking gasolines are in the range 64-70 and depend on the quality of the crude and the cracking temperature regime. Thermal cracking gasolines are the main component in compounding A-66 gasolines and can be added in small amounts to A-72 and A-76 gasolines. It is not useful to add components produced by thermal cracking to higher-octane gasolines in view of their relatively low knock resistance.

Table 22 presents data on the knock resistance of thermal reforming gasolines. These gasolines have higher octane numbers than thermal cracking gasolines. However, owing to the limited rise in the octane number of

Table 23. Antiknock properties of gasolines prepared by catalytic processes /15, 45-47/

Бензин 1	ОЧИМ 2	ОЧММ 3	Ч 4
Бензин каталитического крекинга тяжелого дистиллятного сырья 5			
из ромашкинской нефти 6	83,8	76,2	7,6
из туймазинской нефти 7	87,0	77,8	9,2
Бензин каталитического крекинга легкого сырья из куйбышевских нефтей 8	82,6	74,9	7,7
Бензин каталитического крекинга керосина термического крекинга мазута бакинских нефтей 9	87,6	78,3	9,3
Бензин каталитического риформинга 10			
платформинг обычного режима 11	83,6	77,0	6,6
жесткого 12	96,6	86,0	10,6
Фракция бензина каталитического риформинга (без толуола); платформинг обычного режима 13	76,0	70,4	5,6
Бензин гидроформинга 14	78,6	71,7	6,9
Головная фракция бензина гидроформинга 15	79,1	71,0	5,1
Бензин гидрокрекинга 16	75,0	71,0	4,0

KEY: 1 -- Gasoline
2 -- ONRM
3 -- ONMM
4 -- Sensitivity
5 -- Gasoline from catalytic cracking of distillate stock
6 -- from Romashkinskaya crude
7 -- from Tuymazy crude
8 -- Gasoline from catalytic cracking of light stock from Kuybyshev crudes
9 -- Gasoline from catalytic cracking of kerosene prepared from the thermal cracking of mazut from Baku crudes
10 -- Catalytic reforming gasoline
11 -- usual-regime platforming
12 -- drastic-regime platforming
13 -- Fraction of catalytic reforming gasoline (not containing toluene); usual-regime platforming
14 -- Hydroforming gasoline
15 -- Head fraction of hydroforming gasoline
16 -- Hydrocracking gasoline

Table 24. Antiknock properties of high-octane components of automotive gasolines /15, 47/

Компонент 1	ОЧИМ 2	ОЧММ 3	Ч 4
Фракция 5			
бутановая 6	94,0	89,0	5,0
изобутановая 7	101,0	97,0	4,0
изопентановая 8	93,0	90,0	3,0
пентамиленовая 9	90,0	87,0	3,0
Газовый бензин (фракция 33—103° С) 10	89,0	85,8	3,2
Диизобутилен (изооктилен) 11	100,0	88,0	12,0
Полимерный бензин 12	100,0	85,0	15,0
Алкилат 13	92,0	90,0	2,0
Алкилбензин (широкая фракция алкилата) 14	90,0—94,0	88,0—92,0	2,0—4,0
Толуол 15	115,0	103,0	12,0
Пиробензол 16	102,0	88,0	14,0
Алкилбензол 17	107,0	100,0	7,0
Изооктан технический 18	100,0	100,0	0,0
Продукты изомеризации фракции C_5—C_6 (изомеризат) 19	81,0—87,0	79,0—85,0	2,0—4,0

KEY: 1 -- Component
2 -- ONRM
3 -- ONMM
4 -- Sensitivity
5 -- Fraction
6 -- butane
7 -- isobutane
8 -- isopentane
9 -- pentamylene
10 -- Natural gasoline (33-103° C fraction)
11 -- Diisobutylene (isooctylene)
12 -- Polymer gasoline
13 -- Alkylate
14 -- Alkylgasoline (broad alkylate fraction)
15 -- Toluene
16 -- Pyrobenzene
17 -- Alkylbenzene
18 -- Technical isooctane
19 -- Products of the isomerization of the C_5-C_6 fraction (isomerizate)

the gasolines and a worsening of several other operating properties, thermal reforming has limited application and was used at refineries in our country as a temporary measure to increase the knock resistance of commercial automotive gasolines [44].

Gasolines produced by catalytic cracking have higher knock resistance compared with gasolines obtained by thermal processes. An increase in the knock resistance in this case occurs mainly due to a rise in the content of aromatic and paraffinic hydrocarbons of isostructure in the gasolines.

Catalytic reforming is specifically intended to increase the knock resistance of straight-run gasolines. Reforming is used most extensively with a platinum catalyst -- platforming. It can be carried out in two regimes -- usual and drastic. In the drastic regime the gasoline yield is lower, gas formation is increased, but the gasoline is produced at a higher octane with aromatic hydrocarbon content up to 70-72 percent (Table 23).

Not only the catalytic reforming distillate as a whole, but also its individual fractions remaining after extraction of individual aromatic hydrocarbons can be utilized as automotive gasoline components.

Besides the above-listed "base" gasolines, a number of other, as a rule, high-octane components (Table 24) are used in compounding commercial automotive gasolines [48-50].

One of the most common components is a blend of low-boiling hydrocarbons with various boiling limits. Natural gasoline is the name given to the broad fraction of low-boiling hydrocarbons; narrower fractions in which a particular hydrocarbon predominates are named after the predominant hydrocarbon.

Low-boiling hydrocarbons extracted from straight-run products or products from secondary processes, and also not participating in reactions in alkylation or polymerization (spent butane-butylene, pentane-aniline, and other fractions) are used in compounding commercial automotive gasolines.

All the remaining high-octane components of automotive gasolines are produced by means of three main reactions:

polymerization of olefinic hydrocarbons (polymer gasoline);

alkylation, using olefins, of isoparaffinic or aromatic hydrocarbons (alkylate, alkylbenzene); and

isomerization of hydrocarbons containing five or six carbon atoms (isomerizate).

Table 25. Octane number of blends of gasoline and hydrocarbons /15/ (octane number of pure gasoline 70)

Содержание бензина в смеси, объемн. % 1	Бензол 2			Изопентан 3			Изооктан 4		
	расчетное ОЧ 5	ОЧММ 6	ΔОЧ 7	расчетное ОЧ 5	ОЧММ 6	ΔОЧ 7	расчетное ОЧ 5	ОЧММ 6	ΔОЧ 7
0	—	106	—	—	90	—	—	100	—
90	74	71	−3	72	72	0	73	73	0
80	77	73	−4	74	75	+1	76	76	0
70	81	75	−6	76	78	+2	79	78	−1
60	84	78	−6	78	79	+1	82	81	−1
50	88	82	−6	80	81	+1	85	83	−2

KEY:
1 -- Content of gasoline in blend, percent by vol.
2 -- Benzene
3 -- Isopentane
4 -- Isooctane
5 -- calculated ON
6 -- ONMM
7 -- Δ ON

Fluctuations in the composition of components due to differences in crude and the technology of the processes at various refineries also are reflected in the knock resistance of components.

The ratio of components in commercial automotive gasolines is determined by the requirements imposed on their quality and by the capabilities of the particular oil refinery. When various automotive gasoline components are being blended, one must consider that the knock resistance of the blend is not an additive property. The octane number of a component in the blend can differ from the octane number of this component in the pure form. Each component has its own blending characteristic or, as is commonly called, its blend octane number. Table 25 gives the values of calculated and actual (determined in a single-cylinder engine) octane numbers of blend of gasoline with individual hydrocarbons and Table 26 gives the octane numbers found in blends of various gasolines with catalytic reforming gasoline.

From the data in Table 25 we see that when benzene is added, the octane number of blends is considerably below those that would be anticipated from calculations. For example, a blend of 10 percent benzene and 90 percent gasoline is characterized by an octane number of 71, instead of the 74 expected from additivity. The blend octane number of benzene in this blend proved to be 80, while in the pure form it is 106. The blend

Table 26. Octane numbers of blends of base gasolines with catalytic reforming gasoline /51, 52/

Базовый бензин и метод определения 1	Содержание бензина каталитического риформинга, % 2					
	0	20	40	60	80	100
Бензин термического крекинга 3						
ИМ 4	76,3	82,7	83,2	83,5	83,6	[illegible]
ММ 5	70,7	74,4	75,5	76,1	76,1	[illegible]
Бензин каталитического крекинга 6						
ИМ 4	92,6	88,7	87,7	87,1	85,4	[illegible]
ММ 5	89,6	83,5	80,0	78,9	77,9	[illegible]
Бензин перегонки нефти парафинистого основания 7						
ИМ 4	57,0	81,5	82,0	82,7	83,2	[illegible]
ММ 5	58,0	74,6	76,3	77,1	77,4	[illegible]
Бензин прямой перегонки нефти нафтенового основания 8						
ИМ 4	68,5	82,0	82,3	82,4	82,5	[illegible]
ММ 5	69,0	73,0	73,7	75,0	76,2	76,2

KEY: 1 -- Base gasoline and determination method
2 -- Content of catalytic reforming gasoline
3 -- Thermal cracking gasoline
4 -- RM
5 -- MM
6 -- Catalytic cracking gasoline
7 -- Gasoline from the distillation of paraffin-base crude
8 -- Gasoline from the direct distillation of naphthenic-base crude

octane numbers of isopentane and isooctane are close to their octane numbers when used in pure form. It must be noted that the blend octane numbers of components depend on their content in a blend and can vary over wide limits.

All the above-presented data on octane numbers were obtained for single-cylinder stands and are only approximate when evaluating the knock resistance of commercial automotive gasolines. The actual octane numbers of gasolines AON are determined directly in engines in stand or road conditions (GOST 10373-63).

Table 27 presents some results of estimating the actual knock resistance of three commercial and two experimental gasolines. All the fuels contained no antiknock additives.

The actual octane number of the A-66 commercial gasoline (ONMM-66; ONRM-66) fluctuated from 72 to 61, depending on the engine model, and averaged

Table 27. Actual knock resistance of automotive gasolines in tests on various engines /1/

Двигатель 1	ФОЧ при n, об/мин 2					
	1000	1500	2000	2500	3000	3500
Товарный бензин А-66 (ОЧММ-66; ОЧИМ-66) 3						
ГАЗ-51 4	66	68	64	63	62	—
ГАЗ-20 5	63	62	63	64	63	64
КАЗ-120 6	69	69	68	67	65	—
Товарный бензин А-72 (ОЧММ-72; ОЧИМ-75) 7						
МеМЗ-966 8	80	79	77	76	75	73
«Москвич-407» 9	76	74	73	73	72	69
«Москвич-408» 10	75	72	68	69	70	70
ГАЗ-21 11	75	74	73	73	72	71
ГАЗ-53 12	74	73	73	72	71	70
Товарный бензин А-76 13						
МеМЗ-966ф 14	78	78	76	75	76	76
«Москвич-407» 15	79	80	80	79	77	73
«Москвич-408» 16	81	78	76	73	73	72
ЗИЛ-130 17	77	77	77	75	72	70
ЗИЛ-375 18	77	78	77	76	72	70
ГАЗ-21 19	78	78	76	74	71	67
ГАЗ-53 20	80	79	77	75	73	70
Опытный бензин АИ-86 (ОЧММ-84; ОЧИМ-86) 21						
ЗАЗ-966 22	86	86	85	85	84	83
«Москвич-407» 23	87	87	86	84	83	82
«Москвич-408» 24	85	85	85	85	85	84
ГАЗ-21 25	90	88	86	87	88	88
ЗИЛ-130 26	84	83	82	82	83	84
Опытный бензин АИ-86 (ОЧММ-79; ОЧИМ-86) 27						
ЗАЗ-966 22	86	85	84	83	81	78
«Москвич-407» 23	87	86	84	82	81	80
«Москвич-408» 24	85	85	84	83	82	81
ГАЗ-21 25	87	86	85	85	86	87
ЗИЛ-130 26	84	82	80	77	74	73

/KEY to Table 27, on preceding page/:

1 -- Engine
2 -- AON for indicated n, rpm
3 -- A-66 commercial gasoline (ONMM-66; ONRM-66)
4 -- GAZ-51
5 -- GAZ-20
6 -- KAZ-120
7 -- A-72 commercial gasoline (ONMM-72; ONRM-75)
8 -- MeMZ-966
9 -- Moskvich-407
10 -- Moskvich-408
11 -- GAZ-21
12 -- GAZ-53
13 -- A-76 commercial gasoline
14 -- MeMZ-966
15 -- Moskvich-407
16 -- Mosvich-408
17 -- ZIL-130
18 -- ZIL-375
19 -- GAZ-21
20 -- GAZ-53
21 -- AI-86 experimental gasoline (ONMM-84; ONRM-86)
22 -- ZAZ-966
23 -- Moskvich-407
24 -- Moskvich-408
25 -- GAZ-21
26 -- ZIL-130
27 -- AI-86 experimental gasoline (ONMM-79; ONRM-86)

65.9. The actual octane number of the A-72 commercial gasoline (ONMM-72; ONRM-75) fluctuated from 80 to 68, and average 74.1. The fluctuations in the actual octane numbers for A-76 gasoline (ONMM-76; ONRM-80) were the largest and ranged from 86 to 71, with the average octane number at 78.9 [1].

These investigations showed that in A-72 and A-76 gasolines the actual octane numbers are closer to the octane numbers determined by the Research Method. Some results of studies made of AI-93 gasolines of different origins using engines of new vehicle models are listed in Table 28.

Of interest are the results of investigating the knock resistance of two experimental gasolines. The gasoline had the identical octane number according to the Research Method (86), but different octane numbers when tested by the Motor Method (84 and 79). One gasoline had low sensitivity (2 points), and the other had high sensitivity (7 points). However, for

Table 28. Actual knock resistance of AI-93 gasoline (based on the data of B. P. Kitskiy, L. V. Malyavinskiy, D. M. Aronov, et al.)

Двигатель 1	Оценка в начале испытаний 2			Оценка после пробега 5—7 тыс. км 3			
	ОЧ$_{т}$ 4	ФОЧ * 5	ФОЧ ** 6	ОЧ$_{т}$ * 7	ФОЧ * 8	ОЧ$_{т}$ ** 9	ФОЧ ** 10
ВАЗ-2101 11	90,0	90,0	91,5	91,5	88,5	89,5	91,5
«Москвич-412» 12	93,0	90,0	92,4	91,4	88,8	91,0	91,5
ГАЗ-24 13	86,7	86,0	87,0	86,7	85,0	87,0	87,2

* Ethyl gasoline
** Nonethyl gasoline

KEY: 1 -- Engine
2 -- Rating at beginning of tests
3 -- Rating after a run of 5000-7000 km
4 -- ON_f
5 -- AON *
6 -- AON **
7 -- ON_f *
8 -- AON *
9 -- ON_f **
10 -- AON **
11 -- VAZ-2101
12 -- Moskvich-412
13 -- GAZ-24

most of the engines the actual octane numbers of these two gasolines were very similar (cf. Table 27).

Thus, the gasoline sensitivity in automotive engines is manifested in that the actual gasoline octane number differs from the laboratory value. Here the difference in octane numbers depends on the gasoline's sensitivity and on the specific properties of the given engine and its operating conditions, rated by the knock roughness indicator. This function can be expressed as follows:

$$\Delta \text{AON} = S\ (1 - R/10)\quad [S = \text{sensitivity};\ R = \text{roughness}],$$

where ΔAON = AON -- ONMM; R is the knock roughness of the engine.

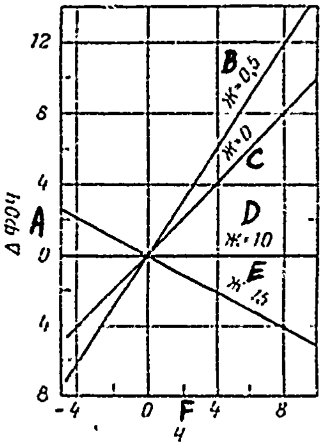

Fig. 43. Effect of fuel sensitivity and knock severity of engine on variation in gasoline octane numbers /42/

KEY: A -- Δ AON
B -- Zh = 0.5
C -- Zh = 0
D -- Zh = 10
E -- Zh = 15
F -- Sensitivity

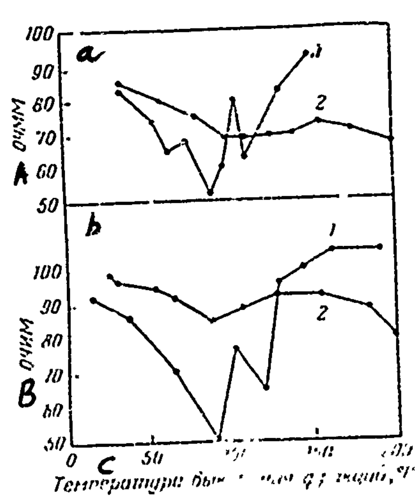

Fig. 44. Knock resistance of fractions of catalytic reforming gasoline (1) and catalytic cracking gasoline (2)

a -- based on the data of Yu. F. Sokov and V. N. Kotova /53/

b -- based on the data of S. N. Bauer and R. Callat /54/

KEY: A -- ONMM
B -- ONRM
C -- Boiling point of fractions

This function is shown in Fig. 43, where we see that in favorable conditions ($R < 0$; $S < 0$), the actual octane numbers can significantly exceed the octane numbers found by the Motor Method. Problems of the fullest use of sensitive fuels are becoming most urgent at the present time since high-octane automotive gasolines produced by a drastic-regime catalytic reforming method have high sensitivities [42].

In recent years, investigators have noted that the actual octane numbers of gasolines are sharply reduced and differ considerably from those obtained in laboratory conditions in the transient operating regimes of automotive engines. This phenomenon is associated with the fractionation of gasoline in the engine intake manifold. At the outset of acceleration of a vehicle, the engine operates at low rpm and with throttle wide open; the pressure in the intake manifold approaches the atmospheric. The flow rate of incoming air is quite low and the gasoline atomizes poorly. Only some of it has sufficiently fine spray and is entrained by the air flow

Table 29. Antiknock properties of 25 percent fractions of straight-run and thermal cracking gasolines

Пределы выкипания фракции, °C 1	Количество фракции, % 2	ρ_4^{20}	ОЧИМ 3	ОЧММ 4
6 Бензин прямой перегонки 5				
Н. к. —90	25	0,6984	83,4	71,7
90—111	25	0,7299	77,6	70,8
111—141	25	0,7587	72,0	65,8
141— к. к. 7	25	0,8013	65,0	56,2
Н. к. — к. к. 8	100	0,7439	75,0	69,3
6 Бензин термического крекинга 9				
Н. к. —84	25	0,7090	78,0	75,8
84—95	25	0,7315	74,5	70,7
95—110	25	0,7455	7[illegible],0	65,6
110— к. к. 7	25	0,7659	6[illegible],2	62,8
Н. к. — к. к. 8	100	0,7396	7[illegible],0	70,8

KEY: 1 -- Boiling limits of fraction
2 -- Amount of fraction
3 -- ONRM
4 -- ONMM
5 -- Straight-run gasoline
6 -- Initial boiling -90
7 -- end boiling
8 -- Initial boiling to end boiling
9 -- Thermal cracking gasoline

directed into the engine cylinders. The larger droplets settle out on the walls of the intake manifold, forming a liquid film.

Low-boiling gasoline hydrocarbons partially evaporate in the intake manifold, and as a result the mixture entering the engine cylinders is enriched in the low-boiling hydrocarbons, while the liquid film is enriched in the high-boiling hydrocarbons. As the throttle is opened, the liquid film along the duct walls will travel at a considerably lower rate than the air flow, and over some time interval a mixture enriched in the low-boiling hydrocarbons will arrive at the cylinders. This phenomenon is temporary, since ultimately the film enters the engine cylinders, ensuring the formation of a mixture with the specified composition.

The phenomenon of gasoline fractionation in the intake manifold has been known for a long time, but until recently it did not cause significant complications in engine operation. The point is that in straight-run and thermal cracking gasolines, low-boiling fractions have higher knock resistance than high-boiling fractions (Table 29).

The octane numbers of fractions are closer together in catalytic cracking gasolines, however even in these gasolines the head fractions have higher knock resistance (Fig. 44). Accordingly, as long as commercial automotive gasolines were compounded on the basis of straight-run and cracking components, their fractionation in the intake manifold did not significantly affect engine operation in transient regimes.

Some fractions in catalytic reforming gasolines have low knock resistance, and the main high-octane components are concentrated in the tail fractions (cf. Fig. 44, Table 30). Therefore when the engine is operated on this gasoline in transient regimes, knocking can be observed because a mixture enriched in low-boiling components with low knock resistance enter the engine cylinders at the outset of acceleration.

Interesting experiments were conducted with three examples of gasoline with the same overall octane numbers, but with different knock resistance for the low-boiling fractions. Determination of the road octane numbers in five motor vehicles in which gasoline fractionation occurred in the intake manifold showed that the knock resistance of low-boiling fractions significantly affects the overall rating of a gasoline in road conditions (Table 31).

A comparison of gasolines of various origins showing that the highest drop in actual knock resistance in fractionation is observed for a blend of catalytic reforming gasoline and straight-run gasoline (10-12 points), a somewhat lower drop -- for the ternary blend of catalytic reforming, catalytic cracking, and straight-run gasolines [8-9], and up to five point reduction for a blend of catalytic reforming and straight-run gasolines [56].

The knock resistance of gasolines when they undergo fractionation in the intake manifold depends strongly on the amount and quality of their antiknocks which are usually unevenly distributed as gasolines are separated into fractions.

Two fundamentally different methods of determining octane numbers in laboratory engines were proposed to allow for the fractionation of gasoline in the intake manifold and to predict the actual knock resistance of a fuel in automotive engines.

The first method consists in rating the knock resistance of any gasoline fraction that has first been distilled in a flask fitted with a standard reflux condenser. Some investigators [57] suggested that the fraction be distilled to 100° C and that its octane number be determined ($ONRM_{100}$). Others [23] proposed distilling 50 or 75 percent of total gasoline and determining the octane number by the Research Method of precisely this part of the gasoline ($ONRM_{50}$ or $ONRM_{75}$).

Table 30. Composition and knock resistance of narrow fractions of drastic-regime catalytic reforming gasoline /48/

Пределы выкипания фракции, °С 1	Количество фракции, % 2	ρ_4^{20}	Содержание ароматических углеводородов, вес. % 3	ОЧИМ 4	ОЧММ 5
Н. к. — 62 6	17,7	0,6331	0	82,4	81,0
62—80	12,0	0,6885	15	65,5	63,4
80—90	3,5	0,7151	23	62,5	61,4
90—100	6,2	0,7375	31	63,8	62,8
100—120	14,1	0,8188	77	97,6	86,6
120—130	3,3	0,8297	80	103,1	89,3
130—140	15,0	0,8553	94	106,9	101,8
140—150	3,0	0,8598	95	101,4	100,0
150—160	6,2	0,8608	96	106,0	98,4
160—170	5,5	0,8689	98	107,7	101,2
170—180	3,5	0,8725	98	106,0	100,0
180—240	3,5	0,8987	98	106,0	92,5
Остаток и потери 7	6,5	—	—	—	—

KEY: 1 -- Boiling limits of fraction
2 -- Amount of fraction
3 -- Content of aromatic hydrocarbons, percent by wt.
4 -- ONRM
5 -- ONMM
6 -- Initial boiling -62
7 -- Residue and losses

Table 31. Effect of knock resistance of low-boiling fractions on the octane number of gasolines /55/

Детонационная стойкость низкокипящих фракций бензинов 1	ОЧДМ при определении на различных автомобилях 2				
Низкая 3	80,2	86,2	87,2	81,5	85,4
Средняя 4	91,0	92,8	91,0	91,4	93,0
Высокая 5	95,0	[illegible]	96,5	94,7	94,0

KEY: 1 -- Knock resistance of low-boiling gasoline fractions
2 -- ONRM /Octane number determined by Road Method/ as determined on various vehicles
3 -- Low
4 -- Middle
5 -- High

The second method provides for additionally equipping the usual unit used in determining octane number by the Research Method with a special insert placed in the intake manifold. The insert can be of different designs, but its function is the same -- to condense and remove the highest-boiling gasoline fractions, that is, to simulate the fraction of gasoline

Table 32. Octane numbers determined by laboratory methods and in road tests for US commercial automotive gasolines [58]

[redacted] 1	Бензины 2													
ОЧ[redacted] 3	101.0	102,1	101,8	101.3	96,8	96,4	96,3	96,4	91,1	91,0	90,4	91,2	98,6	91,1
ОЧ[redacted] 4	90,7	92,5	91,8	88,9	85,2	89,2	89,0	89,3	85,9	85,7	82,8	85,6	90,8	83,1
ОЧ[redacted] 5	93.1	99.5	95,1	98,0	93.8	92,6	82,4	87,0	74,9	87,2	83,4	82,1	85,6	91,8
ОЧ[redacted] 6	99,6	102,2	102,0	102,8	96,7	94,3	93,1	93,3	87,0	89,3	88,6	87,9	96,3	91,3
ОЧ[redacted] 7	−1,4	−0,1	−0,2	−1,5	+0,1	+2,1	+3,2	+3,1	+4,1	+1,7	+1,8	+3,3	+2,3	−0,2
Кол[redacted] ото-бра[redacted]ении ОЧ[redacted] 8	20,2	20,9	21,9	21,7	23,9	20,0	19,2	19,1	15,7	16,3	18,5	15,7	20,3	17,5
ОЧДМ 9	97,6	99,8	99,3	100,8	95,6	93,2	91,3	92,2	87,2	88,7	87,5	88,1	94,4	90,0
ОЧНМ—[redacted] 10	+3,4	+2,3	+2,5	+0,5	+1,2	+3,1	+5,0	+4,2	+3,9	+2,3	+2,9	+3,1	+4,2	+0,5
ОЧИР—[redacted] 11	+2,0	+2,4	+2,7	+2,0	+1,1	+1,0	+1,8	+1,1	−0,2	+0,6	+1,1	−0,2	+1,9	+0,7

KEY: 1 -- Method of octane number determination
2 -- Gasolines
3 -- ON [illegible]
4 -- "
5 -- "
6 -- "
7 -- "
8 -- [Illegible]
9 -- ONR
10 -- ONRM [illegible]
11 -- OND [Distribution octane numbers]

11 -- OND [Distribution octane numbers] [illegible]

directly during the determination of octane numbers [56]. This method came to be called the distribution method, and the octane numbers of gasolines determined by this method are referred to as distribution octane numbers (ONRD).

The data in Table 32 give some idea of the relationship between the octane numbers determined by the various laboratory methods and the low octane number (ONRM).

The low octane numbers, as a rule, correspond more closely to the octane numbers determined by the distribution methods and by other laboratory methods. It must be noted that even the distribution method does not always give satisfactory results.

Noteworthy is the large difference in the octane numbers ONRM_{75} and ONRD, in spite of the relatively small amounts of the fractions entering the engine cylinder in the determination of the octane numbers by these methods. Evidently this difference can be accounted for entirely due to the fact that in the determination of ONRD high-boiling gasoline fractions, owing to atomization, still enter the gasoline cylinder, while in the determination of ONRM_{75} this phenomenon is completely precluded.

At the present time several relationships have been found between octane numbers determined by various methods and the knock resistance of gasolines in road conditions. Some can be represented as follows:

$$\mathrm{ONR} = 0.959 \cdot \mathrm{ONRM} - 0.22\,(\mathrm{ONRM} - \mathrm{ONRM}_{50}) + 3.9$$

$$\mathrm{ONR} = 0.955 \cdot \mathrm{ONRM} - 0.23\,(\mathrm{ONRM} - \mathrm{ONRM}_{100}) + 4.3$$

$$\mathrm{ONR} = \mathrm{ONRM} - 0.363\,(\mathrm{ONRM} - \mathrm{ONRM}_{75}) - 0.131 \cdot S$$

(for ordinary grades of gasolines)

$$\mathrm{ONR} = \mathrm{ONRM} - 0.233\,(\mathrm{ONRM} - \mathrm{ONRM}_{75}) - 0.0113 \cdot S^2$$

(for premium grade gasolines)

Several formulas allowing for the nonuniformity of the distribution of tetraethyl lead and tetramethyl lead have been proposed for gasolines containing antiknock, in addition to those presented above, but this will be discussed in the next section of the book.

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[To Chapter Three]

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CHAPTER FOUR
ANTIKNOCK ADDITIVES

Mechanism of Action

The most effective and economically advantageous method of increasing the knock resistance of automotive gasolines is to add antiknock additives — antiknocks — to them. Antiknocks refer to compounds which when added to gasoline relatively small amounts significantly increase its knock resistance. Efforts to find methods to eliminating knock in internal combustion engines by using antiknocks began about 50 years ago, and at once the high effectiveness of tetraethyl lead (TEL) was found. However, the very significant disadvantage of TEL — its toxicity — compelled efforts for all of these 50 years to continue in searching for other antiknocks that are less toxic than TEL. Several thousands of the most diverse compounds of various classes were tested. Organometallic compounds proved to be the most effective.

Compounds of lead, tin, thallium, bismuth, selenium, tellurium, manganese, iron, cobalt, nickel, copper, chromium, and several other metals exhibit antiknock properties. Alkyls of metals, carbonyls, chelate salts, and "sandwich" structure compounds have been studied as antiknocks [1, 2]. The effectiveness of compounds of lead and manganese will be discussed below; let us dwell only on antiknock properties of compounds of other metals.

Compounds of iron were investigated in close detail and used in practice at one time. Iron pentacarbonyl (IPC) exhibits high antiknock properties. IPC is a pale-yellow liquid, insoluble in water, with a boiling point of 102.5° C and melting point of -21° C. In light the compound decomposes, with the separation of a solid insoluble precipitate $Fe(CO)_9$, which self-ignites on contact with air. Effectiveness of IPC as an antiknock is 15-20 percent lower than TEL.

IPC was used as an antiknock until World War Two in Germany (2-2.5 ml/kg), but then was removed from production. When iron pentacarbonyl is burned, ferric oxide is formed, depositing out in combustion chambers as an easily mobile precipitate with high operative properties. These deposits cause a five to six times increase in engine wear.

All attempts of investigators to find some "scavenger" for the oxides of iron or in some way to neutralize their abrasive action were fruitless. Accordingly, the practice use of iron compounds as antiknock additives is limited at the present time. However, studies on these compounds are still continuing. Recently a diisobutylene-iron pentacarbonyl complex (DIB-IPC) and iron dicyclopentadiene (ferrocene) were tested.

The complex compound iron pentacarbonyl $[Fe(CO)_5]_3 \cdot (C_8H_{16})_5$ exhibits high stability than IPC, but is roughly of the same effectiveness. Ferrocene $(C_5H_5)_2Fe$ is an organic metal compound of the so-called sandwich type. This is an easily sublimated crystalline powder with a melting point of 174° C. Ferrocene exhibits high effectiveness than DIB-IPC and IPC; it increases the octane number of gasolines both with or without TEL. The change to adding ferrocene is faced with the same obstacle as for other compounds of iron -- the absence of effective scavengers for ferric oxide.

Certain chelate salts of copper exhibit high knock resistance. Their effectiveness is close to that of organoiron antiknocks. However, these compounds proved unstable in storage and accelerated oxidation of gasoline hydrocarbons is observed in their presence. Moreover, chelate compounds of copper precipitate on the walls of the intake manifold and cause disturbances in mixture formation, therefore they found no practical use.

Antiknock properties have been noted for compounds such as nicket carbonyl, cobalt 2-ethylhexolate, diethyldiselenide, tetraethyl lead, acetylacetonates of cobalt and of chromium, indium laurate, and others [2-6].

All organometallic antiknocks are added to gasoline in very small amounts, not exceeding tenth and hundredth of a percent. But compounds whose antiknock effect is evident at considerably higher concentrations have also found practical use. Among these the aromatic amines -- derivatives of aniline -- are of leading importance.

Aniline $C_8H_5NH_2$ is a liquid with a boiling point of 184° C and a melting point of -6° C. It is one of the first antiknocks to find practical use. For long time aniline served as a reference standard for rating the antiknock properties of fuels ("aniline equivalent"). A key drawback of aniline is its limited solubility in gasoline. At high aniline contents in gasoline, this compound may precipitate from solution with a drop in temperature. Because of this, aniline itself has not found use as an antiknock, while its derivatives at once were used in a number of countries.

At the close of World War II when TEL production did not meet the growing demand, up to 2 percent xylidine was added to many aviation fuels in the United States and Great Britain. Monomethylaniline was widely used in the FRG in the 1940's-1950's. At one time a blend of aromatic amines with a predominance of monomethylaniline was developed and used in the USSR under the name Ekstralin (GOST 3737-47).

At the present level of the production of aromatic amines and TEL, increasing the octane number by adding TEL proves to be much cheaper than the same increase by adding aromatic amines.

Injecting water into the intake system of an engine is an extremely effective means of suppressing knocking. However, water is not an antiknock. On entering an engine's combustion chambers, it vaporizes, and the vapor is heated with the heat released in the combustion of the mixture. Water injection lowers the temperature in the combustion chambers and cools the cylinder-piston group parts. A reduction of the temperature in the combustion chamber lowers the rate of oxidation reactions preceding knocking and prevents the possibility of knock combustion. Experiments showed that water injection lowers the requirements for the antiknock properties of gasolines by 7-10 octane points.

Water injection was widely tested in domestic vehicles and was used in practice, however, thus far no simple and reliable water injection system has been built. Efforts to find antiknock additives are not rigorous and systematic because there is no single adequately substantiated view of the mechanism of the antiknock action of additives.

Initially the antiknock effect of additives was explained by the action of atomized metal. However, it was soon shown that the introduction of finely dispersed metal particles, in particular, lead, directly into a combustion chamber has only a slight antiknock action. Moreover, various compounds of the same metal prove to differ in effectiveness (in percent):

Tetraethyl lead	100.0	Triphenyl bismuth	18.2
Tetraphenyl lead	59.0	Triphenyl arsenic	1.4
Tetraethyl tin	4.0	Cobalt 2-ethylhexoate	29.0
Dichlorodiethyl lead	67.0	Lead 2-ethylhexoate	5.3
Diethyl selenium	10.0	Lead ethylxanthogenate	7.0
Diethyl tellurium	33.3		

These date made it necessary to attribute some role to the antiknock effect and the organic moiety of additives. However, at the outset of the studies this moiety was attributed only an auxiliary role, since the effectiveness of compounds forming identical organic radicals and different metals in decomposition differed widely.

It was assumed that the organic moiety must be such that the compound as a whole decomposes in the combustion chamber at the required instant and meets all the other requirements imposed on additives.

The auxiliary role of the organic moiety of an antiknock was found to be in agreement also with the initial concepts of the mechanism of antiknock action in the light of the peroxide theory of detonation.

At high temperatures in the combustion chamber antiknocks, including tetraethyl lead, are completely decomposed. Lead and ethyl radicals are formed in the decomposition of TEL:

$$Pb(C_2H_5)_4 \longrightarrow Pb + 4\dot{C}_2H_5$$

The lead formed is oxidized, forming lead dioxide

$$Pb + O_2 \longrightarrow PbO_2$$

which reacts with peroxides, decomposing them:

$$R-CH_2-OOH + PbO_2 \longrightarrow R-COH + PbO + H_2O + \frac{1}{2}O_2$$

Here low-activity oxidation products of hydrocarbons are formed, along with lead oxide. On reacting with air oxygen, lead oxide is again oxidized to lead dioxide, capable of reacting with a new peroxide molecule. Thus, one lead atom, on being reduced and oxidized, is capable of decomposing a large number of peroxide molecules. Each decomposed peroxide molecule, according to the chain theory, must be the initiation for a separate chain of formation of new peroxides. This accounts for the high effectiveness of small amounts of antiknocks.

The fullest exploration of the antiknock action of additives is based on concepts of detonation as the multistage ignition of some of the working mixture. Work by A. S. Sokolik and S. A. Yantovskiy [7] was the first to establish the fundamental difference in the action of TEL in delaying the appearance of cold flame and in delaying the progression of cold-flame processes leading to a hot combustion. It was shown that adding TEL to an air-hydrocarbon mixture sharply weakens the intensity of the primary cold flame (which was recorded by its flow and the pressure increment), prolongs the delay of the secondary flame and, finally, hinders the subsequent explosion, making it possible only at higher pressures [8].

Studies confirmed the main premises of a multistage action of antiknocks [9-17]. Thus, Pastell [9] showed that adding TEL or increasing its concentration has a negligible effect on the onset of the appearance of cold flame and permits subsequent explosion possible at considerably higher pressures; thus, the temperature limits of cold-flame reactions are extended. Sturgis [10] noted that the presence of TEL has a limited effect on the formation of peroxide compounds and hydrocarbon oxidation in the initial stage and causes a breakdown of peroxides, leading to a hot explosion.

Reaction of the antiknock metal on the multistage process is most probably concentrated not in the first, but in subsequent stages in which the presence of atomized metal in the enclosed volume can deactivate active particles formed in the explosive decomposition of the peroxides. The organic radicals appearing during the decomposition of an organometallic antiknock in the combustion chamber facilitate the breakdown of peroxides, proceeding according to a chain mechanism, and lowers the critical concentration for explosive decomposition, thus reducing the intensity of a primary cold flame. And this prevents the inhibition of the further spread of multistage ignition [8].

But the action of free radicals cannot be reduced simply to the general inhibition of the preflame process; free radicals hinder the progression of precisely the low-temperature multistage process, while at the same time facilitating the spread of oxidative reactions characteristic of high-temperature single-stage ignition [8]. It is precisely in this way that A. S. Sokolik [8] explains the reduction in the antiknock effect when there is an increase in the antiknock content in fuel and even a reverse of this effect when at very low tetraethyl lead concentrations the latter begins to act as a knock promoter. In this case it is probable that volumetric single-stage ignition occurs due to the abrupt reduction in the energy of activation resulting from introducing a large number of active initiating centers into the gas.

Thus, the theory of the multistage action of antiknocks attributes an important role both to the metal and to the organic radical, which is in agreement with a great deal of experimental material.

Later work by A. N. Voinov and several other workers [18-25] showed that not all antiknocks have the same mechanism of action. At least two groups of antiknocks differing in mechanism of action were found. One group (including TEL, ferrocene, manganese, cyclopentadienyltricarbonyl) functioned like TEL within the range of cold-flame and hot explosion, while the other group, which includes aromatic amines, and the carbonyls of iron, manganese, and nickel, principally affects the temperature limits of cold flame and to a lesser extent the limits of hot explosion. The action of the second group of antiknocks must be manifested before the appearance of cold flame. There are antiknocks (chelate compounds of copper) that have an intermediate mechanism of action.

A different mechanism of action of antiknock additives containing the same metal was found in studies by A. N. Voinov. This factor once again indicates the active role of the organic moiety of the antiknock.

Thus, the mechanism of antiknock action requires further study, which will permit increasing the effectiveness of existing antiknocks and make it possible to find new ones. We must bear in mind that antiknocks are widely used in all countries and are in a strong first place in terms of volume of commercial production among all gasoline additives.

Compounds of Lead

The most common antiknock is tetraethyl lead (TEL), whose ability to suppress knocking was discovered in 1921 by the engineers Midgley and Boyd (United States). Since February 1923, mass production of this antiknock in the form of ethyl fluid began, which is a blend of TEL and a "scavenger" of the combustion products -- halogen alkyls.

The industrial method of producing tetraethyl lead is based on the reaction of sodium lead alloy with ethyl chloride:

$$4PbNa + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

The starting material for TEL production is sodium chloride, lead, and cracking gases or ethyl alcohol [26].

TEL is a colorless, clear, strongly toxic liquid, heavier than water ($\rho_4^{20} = 1.6524$). Its vapor in small concentration has a sweetish odor; in greater concentrations this compound has an unpleasant odor. It is insoluble in water, but dissolves readily in gasoline, alcohol, acetone, and several other organic solvents. It boils at 200° C with decomposition. When strongly heated, TEL decomposes explosively, forming a black fume consisting of metallic lead.

The antiknock effectiveness of TEL depends on the composition of the hydrocarbon and nonhydrocarbon parts of gasolines. The ability of a hydrocarbon or a gasoline to increase its knock resistance to some extent when antiknocks are added is customarily called response [27].

The response of hydrocarbons to TEL has been studied quite closely and several correlations have been found. Paraffinic hydrocarbons exhibit the greatest response to TEL; olefinic and aromatic hydrocarbons exhibit the least. Naphthenic hydrocarbons are intermediate. And for virtually all hydrocarbons, with the exception of aromatics, the response to TEL decreases with increase in the octane number of the hydrocarbons.

It has also been noted that the first portions of TEL are the most effective. Subsequent addition of TEL increases the octane number of hydrocarbons to a lesser extent. This action of TEL is characteristic for all hydrocarbons, regardless of their structure.

The addition of TEL has different effects on the sensitivity of hydrocarbons. For example, when TEL is added to low-octane paraffinic and naphthenic hydrocarbons, their sensitivity decreases; when TEL is added to paraffinic and naphthenic hydrocarbons with octane number higher than 80, the response increases. The presence of TEL in olefinic and dienic hydrocarbons causes a rise in the sensitivity, while in aromatics it causes a decrease [3].

Table 33. Response of fuels of various origins to TEL /21/

Топливо 1	ОЧИМ 2			ОЧММ 3		
	4 без ТЭС	5 с 0,41 г/кг ТЭС	6 с 0,82 г/кг ТЭС	4 без ТЭС	5 с 0,41 г/кг ТЭС	6 с 0,82 г/кг ТЭС
Бензин прямой перегонки 7						
ромашкинской нефти 8	41,6	49,0	56,0	41,0	50,0	57,0
туймазинской нефти 9	43,0	47,0	53,0	41,0	48,0	[illegible]
краснокамской нефти 10	50,0	56,8	61,4	48,6	56,8	[illegible]
Бензин термического крекинга 11						
гудрона 12	75,2	79,0	80,8	70,0	72,2	[illegible]
полугудрона 13	75,6	80,0	82,9	68,5	70,4	72,0
мазута Новокуйбышевского завода 14	71,2	74,8	77,2	61,2	67,6	71,0
мазута Саратовского завода 15	73,4	75,8	78,3	66,1	69,2	[illegible]
Бензина каталитического крекинга тяжелого дистиллятного сырья 16						
Новоуфимского завода 17	81,8	87,0	89,0	76,1	78,5	[illegible]
Омского завода 18	82,0	85,5	88,0	75,3	78,3	80,0
Бензин каталитического риформинга 19						
обычного режима 20	83,0	86,7	89,0	76,0	81,0	[illegible]
жесткого режима 21	96,0	99,0	100,1	86,0	89,5	91,0
Бензин гидрокрекинга 22	75,0	80,8	85,0	71,0	79,6	[illegible]
Алкилбензин 23	91,0	96,5	98,8	90,0	98,0	[illegible]
Полимербензин 24	100,0	100,0	100,0	[illegible]	[illegible]	[illegible]
Изопентан 25	93,0	99,0	[illegible]	[illegible]	97,0	[illegible]
Пентаамиленовая фракция 26	[illegible]	96,0	100,0	[illegible]	[illegible]	[illegible]

KEY: 1 -- Fuel
2 -- ONRM
3 -- ONMM
4 -- not containing fuel
5 -- containing 0.41 g/kg TEL
6 -- containing 0.82 g/kg TEL
7 -- Straight-run gasoline
8 -- from Romashkinskaya crude
9 -- from Tuymazy crude
10 -- from Krasnokamsk crude
11 -- Thermal cracking gasoline
12 -- from gudron
13 -- from semigudron
14 -- from mazut at the Novokuybyshev Refinery
15 -- from mazut at the Saratov Refinery
16 -- Gasoline from the catalytic cracking of heavy distillate feed
17 -- from the Novoufa Refinery
18 -- from the Omsk Refinery
19 -- Catalytic reforming gasoline
20 -- of usual regime
21 -- of drastic regime
22 -- Hydrocracking gasoline
23 -- Alkyl gasoline
24 -- Polymer gasoline
25 -- Isopentane
26 -- Pentane-amylene fraction

The content of particular hydrocarbons in automotive gasolines determines their response to TEL (Table 33).

Straight-run gasolines usually exhibit greater response to TEL than other gasolines. The difference in response to TEL shown by different gasolines becomes smaller when octane numbers are determined by the Research Method, than by the Motor Method.

Adding TEL as a rule lowers the sensitivity of straight-run gasolines and increases the sensitivity of gasolines prepared by thermal and catalytic processes. Here a general correlation of a decrease in response to TEL with increase in fuel sensitivity is noted [3].

The effectiveness of antiknocks in increasing the knock resistance of gasolines depends to a strong degree on the content and nature of the non-hydrocarbons impurities in gasolines and whether they contain other additives. Compounds affecting the response of gasolines to antiknocks are customarily divided into two groups. The first group includes compounds that lower the response of gasolines to antiknocks — antagonists. The second group includes compounds intensifying the action of antiknocks — — promoters. Sulfur compounds, several halogens, phosphorus compounds, and so on are tetraethyl lead antagonists. Promoters are found among organic acids, esters, and so on [28].

The relationship between gasoline response to TEL and the gasoline content of total sulfur was first noted in 1934-1936 by three different groups of investigators; in the United States [29], Japan [30], and Great Britain [31].

It bears noting that the effect of organic sulfur compounds on the knock resistance of gasolines containing no antiknocks is relatively limited. At concentrations up to 0.05 percent S, organic sulfur compounds have practically no effect on the knock resistance of hydrocarbons. When added in larger concentrations, organic sulfur compounds cause a decrease in octane numbers by 1-2 points (Table 34).

The greatest reduction in octane number is noted when the determination is based on the Motor Method, and the smallest decrease -- for the Research Method; intermediate results are obtained by the method of determining actual octane numbers in full-sized engines (cf. Table 33). Earlier, Rian [33] showed that the octane number of gasolines containing no antiknocks can be reduced by 2.0-2.5 points when tetrasulfides are added (they investigated ter-butyltetrasulfide).

These data suggest that an increase in the octane number of gasolines after hydrofining can only be partially attributed to the removal of organic sulfur compounds. But the main role in this case evidently is played by changes in the chemical composition of the hydrocarbon part of gasolines [32].

Table 34. Effect of Diisopropyl Disulfide on the the Antiknock Properties of B-70 Gasoline Not Containing Antiknocks [28]

Детонационная стойкость 1	Исходный бензин 2	Бензин с диизопропилдисульфидом (0,15% S) 3	Δ ОЧ 4
ОЧИМ 5	71,0	69,8	—1,2
ОЧММ 6	69,2	67,1	—2,1
ФОЧ 7			
1200 *об/мин* 8	67,3	65,9	—1,4
1400 »	68,7	67,0	—1,7
1800 »	69,6	67,7	—1,9
2200 »	69,2	67,8	—1,4
2600 »	68,5	67,3	—1,2

Key: 1 -- Knock resistance
2 -- Initial gasoline
3 -- Gasoline containing diisopropyl disulfide (0.15 percent S)
4 -- Δ ON
5 -- ONRM
6 -- ONMM
7 -- AON
8 -- rpm

Organic sulfur compounds are differentiated by their antagonistic effects on TEL (Table 35).

However, these differences are not so large and the experimental data on all the organic sulfur compounds tested fit in the hatched region between the curves (Fig. 45). On the average, for a sulfur content of 0.05 percent, about half of all of the TEL added is expended nonproductively in reactions with organic sulfur compounds [32, 34].

Among the organic sulfur compounds, the greatest decrease in response to TEL is caused by adding certain mercaptans, disulfides, and polysulfides. A characteristic feature was noted: the fraction of the TEL whose antiknock action is suppressed by an organic sulfur compound remains constant independently of the total TEL concentration in a fuel. And the total TEL amount deactivated by a given amount of sulfur compound increases steadily, while the relative amount remains roughly constant (Fig. 46).

As the concentration of organic sulfur compounds is increased, the antagonistic action intensifies (Fig. 47). However the first portions of the sulfur compounds have the strongest effect.

Table 35. Effect of Organic Sulfur Compounds (0.05 percent S) on the Response of a Blend of 56 percent Isooctane and 44 percent n_5-Heptane to TEL [1]

Образец 1	Показатель 2	Концентрация ТЭС, г/кг топлива 3			
		0,41	0,82	1,23	2,46
Топливо без серы 4	ОЧММ 13	66,0	72,8	76,1	82,0
	А * 13	100	100	100	100
То же топливо с октилмеркаптаном 5	ОЧММ	60,0	65,4	68,5	73,4
	А 13	42	44	42	37
» » с бензилмеркаптаном 6	ОЧММ	59,1	61,7	67,9	71,3
	А 13	36	41	39	40
» » с пропилмеркаптаном 7	ОЧММ	61,0	67,1	70,9	76,1
	А 13	50	53	56	48
» » с изоамилмеркаптаном 8	ОЧММ	62,4	67,3	70,8	77,1
	А 13	60	55	55	53
» » с диэтилсульфидом 9	ОЧММ	61,8	67,2	70,8	77,0
	А 13	56	51	55	52
» » с диизоамилсульфидом 10	ОЧММ	61,6	66,5	69,8	76,0
	А 13	53	50	50	45
» » с дибутилдисульфидом 11	ОЧММ	59,7	65,0	67,9	73,8
	А 13	40	12	39	38
» » с тиофаном 12	ОЧММ	63,0	67,5	70,6	—
	А	65	57	55	—

---

* A = the amount of active TEL, percent, calculated based on the formula $A = (c/c_0) \cdot 100$, where c_0 is the actual concentration of TEL, c is the concentration of TEL, found on the basis of measuring the AON from the curve of response to TEL of this same mixture, but now containing no sulfur compounds.

Key: 1 -- Sample
2 -- Indicator
3 -- Concentration of TEL, g/kg of fuel
4 -- Fuel not containing sulfur
5 -- Fuel as above, containing octylmercaptan
6 -- " , " benzylmercaptan
7 -- " , " propylmercaptan
8 -- " , " isoamylmercaptan
9 -- " , " diethylsulfide
10 -- " , " diisoamylsulfide
11 -- " , " dibutyldisulfide
12 -- " , " thiophan
13 -- ОНММ

The dependence of the loss in gasoline response to TEL on the concentration of organic sulfur compounds was expressed by Rian [33] as follows:

$$\frac{B_0 - B}{B_c} \cdot 100 = k_1 \cdot c^{0.36}$$

where B_0 and B is the response to TEL for a gasoline without sulfur and with sulfur; c is the concentration of the sulfur compounds, percent S·1000; and k_1 is a coefficient; it is 8.9 for mercaptans and disulfides; 6.6 for sulfides; 12.0 for polysulfides; and 4.8 for cyclic sulfur compounds.

Calculations based on the Rian formula agree well with experimental data.

Below are compared the octane numbers (ONMM) of ethyl blends of hydrocarbons in the presence of organic sulfur compounds (mixture 1 — 56 percent isooctane + 44 percent heptane; mixture 2 — 40 percent toluene + 30 percent heptene + 20 percent diisobutylene + 10 percent isooctane):

Sample	Calculated by the Rian formula	Actual
Blend 2 + diethylsulfide (0.05 percent S)	81.7	81.9
Blend 2 + diethylsulfide (0.5 percent S)	78.9	78.9
Blend [no number given] + benzylmercaptan (0.2 percent S)	81.8	82.2
Blend 2 + dibutyldisulfide (0.05 percent S)	80.9	81.2
Blend 1 + thiophan (0.05 percent S)	76.3	76.1
Blend 1 + isoamylmercaptan (0.05 percent S)	61.8	62.4
Blend 1 + octylmercaptan (0.05 percent S)	65.5	65.4
Blend 1 + dibutyldisulfide (0.05 percent S)	65.5	65.0
Blend 1 + dibutylsulfide (0.05 percent S)	70.5	70.8

Using Rian's formula, we can plot a graph of the dependence of loss in response to TEL on the sulfur concentration for any standard gasoline with a mean composition of sulfur compounds (50 percent sulfides, 25 percent mercaptans and disulfides, and 25 percent residual sulfur consisting of thiophenes, thiophans, and polysulfides). The coefficient k_1 for this gasoline is 7.4 and the formula takes on the following form:

$$\frac{B_0 - B}{B_0} \cdot 100 = 7{,}4 \cdot c^{0,36}$$

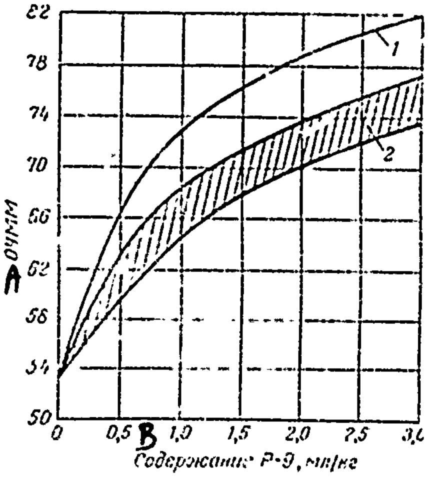


Fig. 45. Effect of organic sulfur compounds on the octane number of a blend of isooctane and heptane for differ ·t TEL content values:

1 -- fuel not containing sulfur
2 -- fuel contains 0.05 % S (the experimental data for all the organic sulfur compounds tested are in the hatched region)

KEY: A -- ONMM
B -- Content of R-9, ml/kg

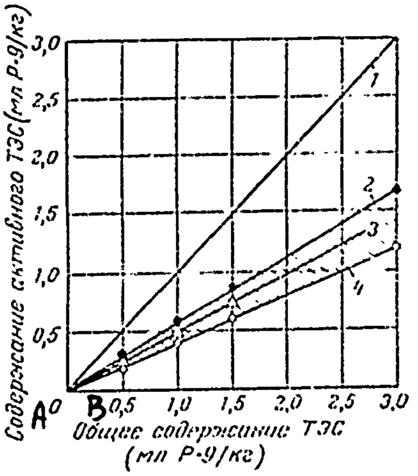


Fig. 46. Dependence of concentration of active TEL on its total concentration ii the fuel:

1 -- containing no sulfur
2 -- containing isoamylmercaptan (0.05 % S)
3 -- mean values for all the organic sulfur compounds tested
4 -- containing benzylmercaptan (0.05 % S)

KEY: A -- Content of active TEL (ml of R-9/kg)
B -- Total content of TEL (ml of R-9/kg)

This function (Fig. 48) can be used in economic calculations aimed at validating the optimal degree of purification of gasoline free of sulfur.

Studies showed [32, 35, 36] that the antagonistic action of organic sulfur compounds does not depend on the hydrocarbon composition of fuels, but depends on the method by which knock resistance is determined.

The decrease in octane numbers in the presence of sulfur compounds, for determination by the more stringent Motor Method, proves to be greater than for determination by the Research Method. In this respect, of interest are the results of determining actual octane numbers in a full-sized engine operating in various regimes [37].

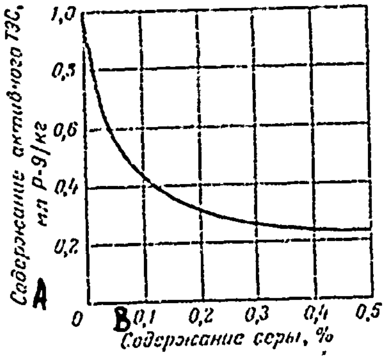


Fig. 47. Effect of benzylmercaptan concentration on the content of active TEL in a blend of hydrocarbons
KEY: A -- Content of active TEL, ml of R-9/kg
B -- Content of sulfur, %

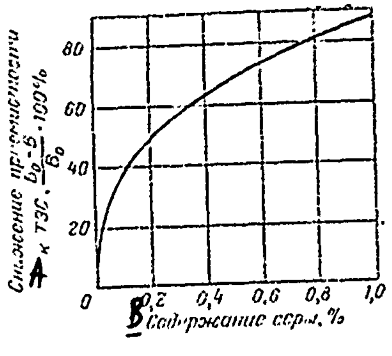


Fig. 48. Dependence of a loss in response to TEL on the sulfur content in gasoline with a mean composition of organic sulfur compounds
KEY: A -- Loss in response to TEL,

$$\frac{B_0 - B}{B_0} \cdot 100\ \%$$

B -- Sulfur content, %

Data on the antagonistic effect of organic sulfur compounds with respect to TEL were fully confirmed even on the full-sized engine (Table 36).

However, it was found that the actual knock resistance of sulfur gasolines containing TEL is lower in a full-sized engine than for the actual knock resistance determined in single cylinder stands, by either the Motor or Research Methods [37]. With an increase in the sulfur concentration in gasoline containing TEL, the actual octane number of the fuel decreases monotonely (Table 37).

The most severe reduction in octane number, just as in laboratory studies, is observed when the first portions of sulfur compounds are added.

The amount of TEL that continues to exert its antiknock functions decreases down to roughly 50 percent, with increase in sulfur content, for sulfur content in the range 0.05-0.1 percent and drops to 20 percent for a sulfur content of 0.3 percent (Table 38).

Table 36. Effect of Organic Sulfur Compounds (0.05 percent S) on the Antiknock Properties of B-70 Gasoline Containing TEL (0.84 g/kg)

Детонационная стойкость 1	Без серы 2	С серой 3	Разность 4
Б-70 + меркаптаны 5			
ОЧИМ 6	83,0	80,1	2,9
ОЧММ 7	81,4	73,6	2,8
ФОЧ 8			
1200 об/мин 9	79,5	74,0	5,5
1400 »	79,2	75,2	4,0
1800 »	80,2	77,2	3,0
2200 »	79,8	78,0	1,8
Б-70 + сульфид 10			
ОЧИМ 6	83,0	81,3	1,7
ОЧММ 7	81,4	79,7	1,7
ФОЧ 8			
1200 об/мин 9	79,5	75,6	3,9
1400 »	79,2	76,0	3,2
1800 »	80,2	76,4	3,8
2200 »	79,8	76,0	3,8
Б-70 + дисульфид 11			
ОЧИМ 6	83,0	80,4	2,6
ОЧММ 7	81,4	77,9	3,5
ФОЧ 8			
1200 об/мин 9	79,5	75,5	4,0
1400 »	79,2	76,0	3,2
1800 »	80,2	76,5	3,7
2200 »	79,8	75,4	4,4

Key: 1 -- Knock resistance
2 -- Not containing sulfur
3 -- Containing sulfur
4 -- Difference
5 -- B-70 gasoline + mercaptans
6 -- ONRM
7 -- ONMM
8 -- AON
9 -- rpm
10 -- B-70 gasoline + sulfide
11 -- B-70 gasoline + disulfide

There are several points of view concerning the mechanism of the antagonistic action of organic sulfur compounds with respect to antiknocks. The main disagreements pertain to the question of what is dominant in the antagonistic effect: the reaction of sulfur compounds with TEL in preflame reactions in the combustion chamber, or low-temperature reactions between these compounds in storage and use.

Table 37. Effect of Diisopropyl Disulfide Concentration on the Antiknock Properties of Gasoline Containing TEL (0.84 g/kg)

Детонационная стойкость 1	0,0% S	0,05% S	0,10% S	0,15% S	0,30% S
ОЧИМ 2	83,0	80,4	78,8	77,4	75,5
ОЧММ 3	81,4	77,9	76,0	74,9	72,5
ФОЧ 4					
1200 об/мин 5	79,5	75,5	75,4	73,0	70,0
1400 »	79,2	76,0	76,0	74,5	71,0
1800 »	80,0	76,5	76,0	74,2	71,5
2200 »	79,8	75,4	74,5	73,5	72,0

Key: 1 -- Knock resistance
2 -- ONRM
3 -- ONMM
4 -- AON
5 -- rpm

The results of recent work [32, 28] permit the statement, with certainty, that the antagonistic effect of organic sulfur compounds is a consequence of reactions occurring in the gaseous phase in the preflame stages of the combustion product. The direct reaction of some compounds at low storage and use temperatures, even if actually occurring, do so very slowly and are of secondary importance in the overall antagonistic effect of organic sulfur compounds. The reduction in knock resistance in the preflame period can be represented as follows.

Under the peroxide theory of detonation following the chain mechanism, the action of TEL can be represented as follows:

$$ROO\cdot + PbO_2 \rightarrow PbO + RO + O_2$$

$$PbO + 1/2O_2 \rightarrow PbO_2 \quad \text{and so on.}$$

The action of organic sulfur compounds evidently consists in breaking the reaction chain by reacting with active lead compounds:

$$PbO + R_1S \rightarrow PbS + R_1O$$

Evidently, it is not the actual sulfur compound molecules that participate in the same reactions, but their thermal decomposition products. Thus, the antagonistic action of sulfur compounds with respect to TEL must be determined not by the chemical activity of the molecules, but by their thermal stability in the combustion chamber conditions. In favor of this hypothesis is also the fact that in spite of the large difference in chemical activities of organic sulfur compounds such as mercaptans and sulfides, their antagonistic action with respect to TEL differs only slightly.

Table 38. Amount of "Active TEL" (in percent) Remaining in Gasoline After the Addition of Diisopropyl Disulfide at Various Concentrations

Детонационная стойкость 1	Количество «активного ТЭС» при концентрации серы 2			
	0.05%	0.1%	0.15%	0.3%
ОЧИМ 3	59	46	36	22
ОЧММ 4	48	34	27	14
ФОЧ 5				
1200 об/мин 6	57	56	40	20
1400 »	50	48	39	17
1800 »	47	45	36	16
2200 »	48	42	33	22

Key: 1 -- Knock resistance
2 -- Amount of "active TEL" at indicated sulfur concentration
3 -- ONRM
4 -- ONMM
5 -- AON
6 -- rpm

We know that an increase in the number of sulfur atoms in a molecule $R(S)_nR'$ causes a weakening of bonds and promotes the thermal decomposition of the compound. The decomposition of organic sulfur compounds increases from monosulfides to disulfides and further to polysulfides. It is in exactly this same sequence that these compounds are ranked also in experimental determinations of their antagonistic action.

Obviously, sulfides and disulfides includes some compounds, which depending on the nature and size of the hydrocarbon portion of the molecule, can differ widely in thermal stability, and therefore, also in antagonistic action. And so, the stronger antagonism of disulfides compared with sulfides can be noted only as a general correlation; some representatives of the sulfides can have a stronger action than some disulfides.

Earlier it was stated that the fraction of TEL whose antiknock action is suppressed by a sulfur compound remains constant, independently of the total TEL concentration in the fuel. This phenomenon can be explained evidently by the mechanism of preflame reactions and, in particular, in the characteristics of TEL decomposition and in the reactivity of its decomposition products. A study of the behavior of various organic sulfur compounds in ethyl gasolines can provide additional material for the study of the mechanism of TEL antiknock action.

Table 39. Effect of Organic Chlorides on the Octane Number of Ethyl Isooctane /38/; the Octane Number of the Pure Product is 113.5

Соединения хлора 1	Содержание хлора в продукте, % 2	ОЧММ с Р-9 (3 мл/кг) 3	ΔОЧ 4
н-Пропилхлорид 5	0,1000	112,1	—1,4
н-Бутилхлорид 6	0,1000	112,7	—0,8
трет-Бутилхлорид 7	0,1000	105,4	—8,1
н-Амилхлорид 8	0,1000	112,0	—1,5
трет-Амилхлорид 9	0,0009	113,5	0,0
трет-Амилхлорид 9	0,0092	112,9	—0,6
трет-Амилхлорид 9	0,0922	104,0	—9,5

Key:
1 -- Chlorine compcunds
2 -- Content of chlorine in product, %
3 -- ONMM containing R-9 (3 ml/kg)
4 -- Δ ON
5 -- n-Propylchloride
6 -- n-Butylchloride
7 -- ter-Butylchloride
8 -- n-Amylchloride
9 -- ter-Amylchloride

Besides organic sulfur compounds, several compounds of chlorine (Table 39), bromine, phosphorus, and so on [2] have an antagoniscit action toward TEL.

Compounds of chlorine, bromine, and phosphorus are not contained in gasolines, however they can be used as additives and may be added to gasoline to improve the removal of lead and to reduce the glowing ignition. But they are added for these purposes in amounts that are so small that the reduction in the octane number does not exceed one point.

A great many compounds have been tested as products promoting (enhancing) TEL action, but organic acids and esters are the most effective [39]:

	Concentration, mg·mole/kg	Δ ON
Carboxylic Acids		
Acetic	50	2.0
Propionic	50	2.3
Butyric	44	2.3
Oleic	80	2.3

[Display continued on following page]

Trimethylacetic	50	1.7
Acrylic	80	2.6
Crotonic	46	2.0
Benzoic	50	2.1
Formic	43	0.2
Pyruvic	80	-0.6
Salicylic	24	-1.6
Esters		
Acetylglycol	44	1.4
ter-Butylacetate	60	0.9
ter-Butylpropionate	77	0.9
ter-Butylbenzoate	56	1.4
ter-Butylnitroacetate	50	-3.2
ter-Amylacetate	80	0.9
Derivatives of Carboxylic Acids, and Other Compounds		
Acetic anhydride	80	1.9
Butyric anhydride	80	1.6
Aniline propionate	60	2.5
Pyridine acetate	80	2.6
Benzoic anhydride	50	0.0
Benzaldehyde	94	0.0
Butyric aldehyde	56	-0.1
Propionic aldehyde	93	0.9

The addition of acids increases the antiknock resistance only of ethyl gasolines. In the absence of TEL, acids do not affect the octane numbers of gasolines (Fig. 49). As the TEL content in gasolines is increased, the effectiveness of the action of acids is enhanced and the optimal acid concentration rises. Adding an acid to high-octane gasolines is more effective than adding it to low-octane gasolines. The promoting action of acids rises with increase in gasoline oxygen numbers.

The effectiveness of acids depends also on gasoline composition. An increase in the content of aromatic hydrocarbons in a gasoline leads to a rise in the effect achieved by adding acids (Fig. 50).

When monocarboxylic acids are added, certain operating properties of a gasoline are degraded (corrosiveness, ability of the additive to be washed out with water, and so on), therefore, only their derivatives can be used in practice.

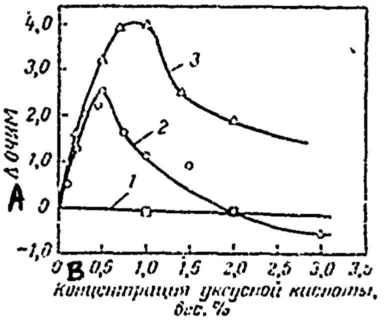


Fig. 49. Effect of acetic acid concentration on the knock resistance of gasoline; the gasoline contains 43 percent aromatic, 16 percent olefinic, and 41 percent paraffinic and naphthenic hydrocarbons; its octane number is 99.5:

1 -- not containing TEL
2 -- containing 0.8 ml TEL/l
3 -- containing 1.6 ml TEL/l
Key: A -- Δ ONMM
B -- Acetic acid concentration, percent by weight

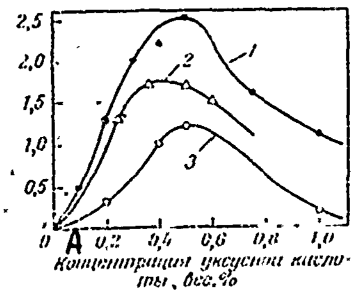
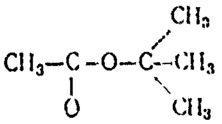


Fig. 50. Effect of acetic acid concentration on the knock resistance of gasolines with various content of aromatic hydrocarbons (initial octane number of all gasolines was 100) [39]:

1 -- 43 percent aromatic hydrocarbons
2 -- 36 percent "
3 -- 29 percent "
KEY: A -- Concentration of acetic acid, percent by weight

Based on chemical and physical properties for extensive and comprehensive studies, ter-butylacetate was selected; upon thermal composition, it yields acetic acid and isobutylene. It was established that compounds manifesting their activity only after decomposition are less effective than the initial acids (Fig. 51).

ter-Butylacetate is a colorless liquid, easily miscible with gasolines in any ratios. This compound is stable, nontoxic, does not cause corrosion, is miscible with other additives, does not attack paint and varnish coatings, rubber, and so on. Below are presented the physical properties of ter-butylacetate:

Structure	
Molecular weight	116
Temperature, ° C	
boiling point	96
flash point (in closed crucible)	Below 0
cloud point	Below -60
melting point	Below -60

[Display continued on following page]

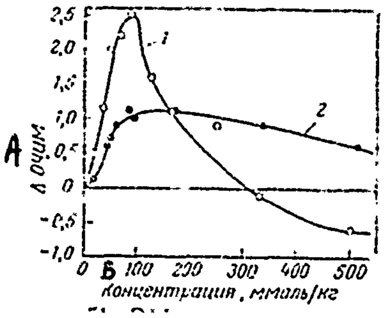


Fig. 51. Effectiveness of acetic acid (1) and ter-butylacetate (2)
KEY: A -- Δ ONRM
B -- Concentration, mmole/kg

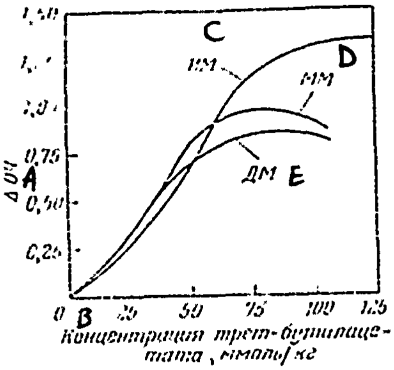


Fig. 52. Effectiveness of ter-butylacetate based on various methods of rating octane number /39/

KEY: A -- Δ ON
B -- Concentration of ter-butylacetate, mmole/kg
C -- RM
D -- MM
E -- R /Road Method/

ρ_4^{20}	0.866
Index of refraction	1.3870
Solubility in water at 26.7° C, percent	0.62

The highest increase in octane number upon the addition of ter-butylacetate is observed when the knock resistance is rated by the Research Method (Fig. 52).

The effectiveness of ter-butylacetate depends on the engine operating regime (Table 40).

An increase in the TEL concentration in a gasoline (Fig. 53) and an increase in the octane numbers of base gasolines (Fig. 54) leads to a rise in the effectiveness of ter-butylacetate. On the average, the optimal concentration of ter-butylacetate in gasoline is 0.75 percent by volume (cf. Fig. 54).

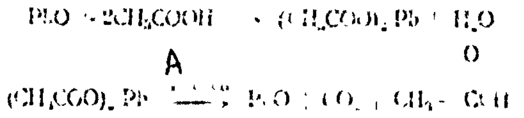
The mechanism of the promoting action of monocarboxylic acids and their derivatives has not been established. One of the explanations of this effect is based on the following assumptions. The decomposition of TEL in a com-

Table 40. Effectiveness of ter-Butylacetate as an Antiknock (ONR) as a Function of Engine Crankshaft Rpm /40/

1 n, об/мин	2 без присадки	3 [illegible]	4 [illegible]
1000	91,7	95,1	3,4
2200	91,8	92,3	0,5
2500	90,6	92,1	1,5
3000	90,2	91,9	1,7

KEY: 1 -- n, rpm
2 -- Not containing additive
3 -- containing 0.5 percent by volume ter-butylacetate
4 -- ΔON

bustion chamber occurs rapidly and long before the buildup of predetonation reactions. After a decomposition of TEL, its decomposition products are subjected to agglomeration; the degree of dispersion is reduced and the active surface is diminished. With increase in the engine compression ratio and with a rise in the knock resistance of a gasoline, the discontinuity in time between the TEL decomposition and the instant of the greatest buildup of reactions leading to detonation steadily rises. These additives obviously prevent the agglomeration of TEL decomposition products by retaining their effectiveness up to the required instant. The possible sequence of reactions in which carboxylic acids can participate in regenerating lead oxide can be seen with the example of the production of ketones by the high-temperature decomposition of the corresponding salts:



$$PbO + 2CH_3COOH \rightarrow (CH_3COO)_2Pb + H_2O$$

$$(CH_3COO)_2Pb \xrightarrow{A} PbO + CO_2 + CH_3-\overset{O}{C}-CH_3$$

KEY: A -- heating

It can be assumed that in this case the agglomeration of lead oxide is hindered and the compound remains in the active state for a longer time.

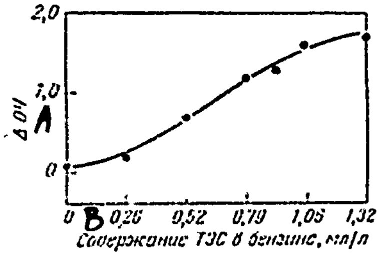


Fig. 53. Effect of adding 0.7 percent ter-butylacetate on the Δ ON of gasoline for various TEL concentrations /41/

KEY: A -- ΔON
B -- Content of TEL in gasoline, ml/l

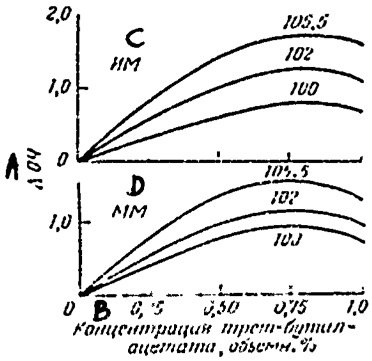


Fig. 54. Effect of ter-butylacetate concentration on the Δ ON of automotive gasolines /41/; the numbers alongside the lines are the octane numbers of the gasolines

KEY: A -- ΔON
B -- Concentration of ter-butylacetate, percent by volume
C -- RM
D -- MM

At the present time, ter-butylacetate is used in the United States to enhance the knock resistance of premium ethyl gasolines. The stock for its production (isobutylene and acetic acid) is not in short supply; synthesis represents no difficulties.

In recent years, researchers' attention has been directed to another organic compound of lead -- tetramethyl lead (TML). At one time, in research done on tetraethyl lead, the antiknock properties of other lead alkyls were also studied. However, at that time TEL proved to be the most effective compound. At the present time, owing to the changes in gasoline composition (increase in content of aromatic hydrocarbons) and increase in automotive engine compression ratios (increase in the octane number of gasolines), it was necessary to turn again to studying alkyl lead compounds. It was found that in high-octane aromatized automotive gasolines, TML is more effective than TEL [42-48].

The higher effectiveness of TML is evidently due to its higher thermal stability and to its stability to be decomposed into active radicals at higher temperatures. Temperature conditions in modern uprated engines with high compression ratios have significantly risen, especially owing to the use of high-aromatized gasolines. Whereas an old engine with low thermal stresses, TEL decomposed at the most appropriate instant, while TML lagged, in new engines, in more severe temperature conditions, TEL evidently decomposes too early, therefore some of the active radicals formed are expended nonproductively, without breaking the chains of preflame reactions leading to detonation. Tetromethyl lead, owing to its higher thermal stability, decomposes in modern engines most likely at the instant of the greatest buildup of predetonation reaction.

Replacing TEL with an equivalent amount of TML (based on the metal content) increases octane numbers by several points (Table 41).

The greatest effect of TML is achieved when the antiknock properties are rated in road conditions, and the least -- when octane numbers are determined by the Motor and Research methods.

The relative effectiveness of TML increases with increase in the aromatic hydrocarbon content in gasolines (Table 42).

It is assumed that TML is more effective to use than TEL in gasolines containing more than 30 percent aromatic hydrocarbons. The effectiveness of TML depends not only on the total aromatic hydrocarbon content, but also on the structure of this class of compounds. However, no correlations have yet been established in this case.

A major advantage of TML compared with TEL is its lower boiling point and its higher saturated vapor pressure:

	TEL	TML
Molecular weight	323.45	267.35
ρ_4^{20}	1.652	1.995
Boiling point, ° C	200	110
Melting point, ° C	-130	-28
P_{sat} at 20° C, mm Hg	0.3	26.5

This advantage of TML is reflected especially strongly in the engines which have a considerable nonuniformity in the distribution of gasoline fractions by engine cylinders. In engines of this kind, high-boiling TML enters with the tail gasoline fractions and arrives in greater amount in the cylinders where more liquid film enters. TML, with higher volatility, is more uniformly distributed by cylinders, which ensures better utilization of the gasoline's antiknock properties.

The superior volatility of TML is a particularly valuable quality when an engine is being operated in variable regimes and, in particular, in engine acceleration. Earlier it was noted that when a speed throttle

Table 41. Antiknock Effectiveness of Alkyl Lead Compounds Determined by Various Methods (Composition of Fuel: 50 Percent Heavy Reforming Gasoline, 30 Percent Alkylate, and 20 Percent Isopentane)

Продукт 1	ОЧИМ 2	ОЧММ 3	ОЧИР 4	ОЧИМ₇₅ 5	ОЧДМ 6
Бензин без ТЭС 7	96,2	86,9	95,1	94,7	98,0
Бензин с ТЭС * 8					
0,37	100,1	91,4	99,7	96,6	–
0,74	102,1	94,3	102,1	98,0	102,1
1,11	103,1	95,6	103,2	98,6	104,0
1,48	103,9	97,1	101,5	99,3	105,0
Бензин с ТМС * 9					
0,37	99,6	91,8	99,8	99,1	--
0,74	102,2	95,5	101,2	102,0	104,9
1,11	103,4	96,8	106,0	103,5	106,7
1,48	101,3	98,0	107,9	101,7	107,6
Бензин с 50% ТЭС + 50% ТМС * 10					
0,37	100,3	92,2	99,9	97,9	--
0,74	102,3	94,2	103,4	100,7	103,6
1,11	103,2	95,8	105,1	101,9	107,1
1,48	104,1	96,6	106,4	102,8	106,6
Бензин с диэтилдиметилсвинцом * 11					
0,37	100,7	92,1	99,8	98,5	
0,74	102,5	94,2	103,3	100,7	10[illegible],8
1,11	103,4	95,9	104,9	102,0	105,8
1,48	104,3	97,3	106,2	102,8	10[illegible],8

---

* The concentration is expressed in g Pg/kg fuel.

KEY:
1 -- Product
2 -- ONRM
3 -- ONMM
4 -- ONDM /Distribution Method Octane Number/
5 -- ONRM$_{75}$
6 -- ONR
7 -- Gasoline containing no TEL
8 -- Gasoline containing TEL *
9 -- Gasoline containing TML *
10 -- Gasoline containing 50 percent TEL + 50 percent TML *
11 -- Gasoline containing diethyldimethyl lead *

Table 42. Effect of Aromatic Hydrocarbons in Gasolines on the Relative Effectiveness of TML /42/

Концентрация ароматических углеводородов, % 1	ОЧ с 0,8 мл/л ТЭС 2		ΔОЧ бензинов с ТМС 5		
	ИМ 3	ММ 4	ИМ 3	ММ 4	ДМ 6
48,1	101,7	96,3	0,3	1,4	2,1
43,0	100,5	88,2	0,3	0,8	1,0
39,0	100,3	90,5	0,5	0,6	1,6
35,0	99,4	88,1	0,1	0,7	0,9
32,0	99,3	87,8	−0,1	0,7	0,8
28,0	98,8	86,6	0,5	0,5	0,5
6,0	99,2	87,4	−1,6	0,1	0,6

KEY: 1 -- Concentration of aromatic hydrocarbons
2 -- ON for gasoline containing 0.8 ml/l of TEL
3 -- RM
4 -- MM
5 -- Δ ON of gasolines containing TML
6 -- R /Road Method of Octane Number determination/

is opened abruptly, first an air-gasoline mixture with a low content of heavy fractions enters into the combustion chambers. The liquid film in which most of the TEL is concentrated builds up its flow rate slowly, and for the same period of time a mixture lean in TEL reaches the cylinders, that is, a mixture with poorer antiknock properties. Thus, at the instant of the initial acceleration of the vehicle at relatively low rpm when the engine imposes the heaviest antiknock requirements on the gasoline, a mixture with low antiknock properties reaches the combustion chambers. In these cases, peak operation of an engine with fairly intense knocking is possible, which leads to premature wear of parts.

Tetramethyl lead is distributed for uniformity between the vapor and liquid phases and therefore when a vehicle is being accelerated, a mixture containing a greater amount of the antiknock, that is, with superior antiknock qualities, reach the combustion chambers.

To improve the distribution of antiknock, tests were made of the antiknock properties not only of TEL and TML, but also of their blends, as well as of compounds such as triethylmethyl lead, diethyldimethyl lead, and ethyltrimethyl lead. The saturated vapor pressure of these compounds and blends is higher than that of TEL:

	Lead Content, percent by weight	Relative Saturated Pressure at 20° C
TEL	64.06	1
75 percent TEL + 25 percent TML	66.97	25
Triethylmethyl lead	66.97	5
50 percent TEL + 50 percent TML	70.15	51
Diethyldimethyl lead	70.15	17
25 percent TEL + 75 percent TML	73.64	75
Ethyltrimethyl lead	73.64	45
TML	77.51	100

Physical mixtures of TEL and TML are more volatile than the corresponding tetraalkyls with dissimilar radicals.

Of interest are the results of comparing the antiknock properties of the gasoline containing TEL, TML, and other tetraalkyls of lead using various methods of octane number determination (Table 43).

Benzene has the same octane number, when containing all antiknocks, determined by the Research Method. The octane number of the fraction boiling to 100° C is higher when physical blends of TEL and TML are used, which are a consequence of a superior volatility of the physical mixtures. Here the use of TML gives an octane number nearly 10 points higher than TEL. The distribution octane number also proved to be highest when TML was used.

A study of the antiknock properties of tetraalkyls and their mixtures in road conditions showed that physical blends of TEL and TML in which TML predominates are the most effective (Table 44).

When an engine is being operated on a gasoline containing TML, phosphorus additives more easily suppress glowing ignition caused by deposits than when the engine is being run on a gasoline containing TEL. Here the optimal phosphorus additive concentration is considerably less.

TML is virtually equivalent to TEL in its effect on other operating properties of gasolines. The cost of TML at the present time is somewhat higher than the cost of TEL, however this compound is already being produced on a commercial scale and is used in many countries.

Compounds of manganese

In 1951 organometallic compounds were synthesized whose molecules represent a "sandwich" with a transition metal atom, situated between two cyclopentadienyl rings. In 1954 Fischer and Jira were the first to

Table 43. Antiknock Properties of Gasoline /47/ Containing Various Lead Compounds (Concentration of Tetraalkyls of Lead Is Chosen so as to Ensure the Same Octane Numbers for the Gasoline as Determined by the Research Method)

Показатель 1	ТЭС 2	Смесь А* 3	Смесь Б* 4	Смесь С* 5	ТЭС + ТМС 6			ТМС 10
					75% ТЭС 7	50% ТЭС 8	25% ТЭС 9	
ОЧИМ 11	92,4	92,4	92,4	92,4	92,4	92,5	92,5	92,4
ОЧММ 12	86,0	85,9	86,0	86,1	86,0	86,0	86,2	86,3
ОЧИМ$_{100}$ 13	74,7	74,5	74,5	74,5	74,5	76,6	80,3	81,2
ОЧИР 14	88,2	87,4	88,0	88,0	88,0	88,3	89,7	91,0
Содержание свинца в бензине, г Pb/л 15	0,52	0.48	0,47	0,51	0,51	0,51	0,55	0,65
Содержание свинца по фракции до 100° С, г Pb/л 16	17 Отс.	17 Отс.	0,02	0,08	0,08	0,16	0,28	0,41

---

* Composition of mixture, percent by weight

KEY: 1 -- Indicator
2 -- TEL
3 -- Blend A *
4 -- Blend B *
5 -- Blend C *
6 -- TEL + TML
7 -- 75 percent TEL
8 -- 50 percent TEL
9 -- 25 percent TEL
10 -- TML
11 -- ONRM
12 -- ONMM
13 -- ONRM$_{100}$
14 -- ONDM
15 -- Lead content in gasoline, g Pb/l
16 -- Lead content in fraction to 100° C, g Pb/l
17 -- Absent

	ТЭС 1	Триэтилметилсвинец 2	Диэтилдиметилсвинец 3	Этилтриметилсвинец 4	ТМС 5
A	31	[illegible]	[illegible]	[illegible]	1
B	6	[illegible]	[illegible]	[illegible]	6
C	1	[illegible]	[illegible]	[illegible]	31

KEY: 1 -- TEL 2 -- Triethylmethyl lead
3 -- Diethyldimethyl lead 4 -- Ethyltrimethyl lead
5 -- TML

Table 44. Antiknock Effectiveness of Tetraalkyls of Lead in the Determination of the Road Octane Number [44]

Показатель 1	Триэтилметилсвинец 2	Диэтилдиметилсвинец 3	Этилтриметилсвинец 4	ТЭС + ТМС 5			
				75% ТЭС 6	50% ТЭС 6	25% ТЭС 6	ТМС 7
Число автомобилей 8	3	8	3	1	8	4	5
Количество оценок 9	48	184	48	15	173	86	85
Среднее повышение эффективности по сравнению с ТЭС, ДОЧДМ 10	0,02	0,39	0,16	0,24	0,54	0,80	0,42
Процент случаев, когда ОЧ повышалось 11							
на 0,1 пункта и более 12	47	83	66	66	82	84	75
» 0,5 » » » 13	14	50	29	26	62	77	50

KEY:
1 -- Indicator
2 -- Triethylmethyl lead
3 -- Diethyldimethyl lead
4 -- Ethyltrimethyl lead
5 -- TEL + TML
6 -- TEL
7 -- TML
8 -- Number of motor vehicles
9 -- Number of ratings
10 -- Mean rise in effectiveness compared with TEL, ONR
11 -- Percentage of cases when the ON was increased
12 -- by 0.1 point and higher
13 -- by 0.5 point and higher

prepare cyclopentadienyltricarbonyl manganese (CTM). The authors established that dicyclopentadienyl manganese, when heated under carbon monoxide pressure, is converted into a yellow, easily sublimated crystalline product having the composition $C_5H_5Mn(CO)_3$. The resulting compound is a "half-sandwich" with a manganese atom in its center [50-58].

The first reports of the discovery of antiknock properties for the new manganese compounds appeared in the press in 1957 [59, 60].

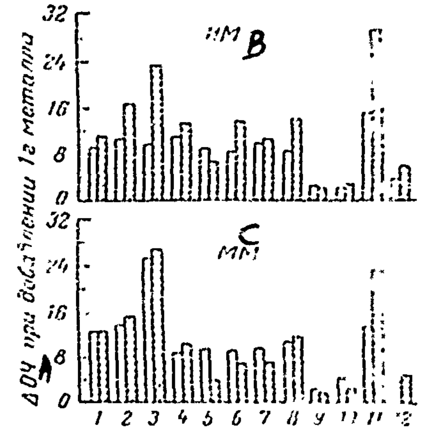


Fig. 55. Response to MCTM (hatched) and to TEL shown by pure hydrocarbons:

1 -- 2,2-dimethylbutane
2 -- 2-methylpentane
3 -- n-heptane
4 -- 2,4-dimethylpentane
5 -- triptane
6 -- 2,2,4-trimethylpentane
7 -- cyclohexane
8 -- methylcyclohexane
9 -- 2-methylbutene-2
10 -- diisobutylenes
11 -- octene-1
12 -- ethylbenzene

KEY: A - Δ ON upon the addition of
1 g metal
B -- RM
C -- MM

Over the past several years, "sandwich" compounds of several other metals were synthesized and their antiknock properties investigated [61-66]. Among the compounds tested, the most effective proved to be compounds of manganese -- cyclopentadienyltricarbonyl manganese (CTM) and methylcyclopentadienyltricarbonyl manganese (MCTM) (Table 45).

All the main research and tests abroad were conducted on methylcyclopentadienyltricarbonyl manganese, $CH_3C_5H_4Mn(CO)_3$, which is known in the chemical industry by the designation MD-DMT, and in the petroleum industry as AK-33Kh [67-86]. This compound is a clear low-viscous, light-amber

Table 45. Antiknock Effectiveness of Several Organometallic Compounds /66/

Соединение 1	2 ОЧИМ с добавкой соединения	3 ΔОЧ
4 Дициклопентадиенилникель (никелоцен) $Ni(C_5H_5)_2$	58	13
5 Дициклопентадиенилдикарбонил никеля $Ni_2(C_5H_5)_2(CO)_2$	59	18
6 Трициклопентадиенилдикарбонил никеля $Ni_3(C_5H_5)_3(CO)_2$	43	1
7 Ацетилацетонат никеля $Ni(C_5H_7O_2)_2$	47	7
8 Ацетилацетонат кобальта $Co(C_5H_7O_2)_2$	53	8
9 Ацетилацетонат железа $Fe(C_5H_7O_2)_3$	46	6
10 Пентакарбонил железа $Fe(CO)_5$	50	10
11 Дициклопентадиенилжелезо (ферроцен) $Fe(C_5H_5)_2$	61	14
12 Диметилферроцен $Fe(C_5H_4CH_3)_2$	56	11
13 Тетрациклопентадиенилдикарбонилжелезо $Fe_2(C_5H_5)_4(CO)_2$	49	9
14 Диацетилферроцен $Fe(C_5H_4COCH_3)_2$	50	5
15 Дициклопентадиенилрейнекат железа $Fe(C_5H_5)_2[Cr(SCN)_4(NH_3)_2]$	49	9
16 Дициклопентадиенилтетрафенилборат железа $Fe(C_5H_5)_2[B(C_6H_5)_4]_2$	49	9
17 Диэтилциклопентадиенилтетрафенилборат железа $Fe(C_7H_9)_2[B(C_6H_5)_4]_2$	47	7
18 Дитетрагидроинденилтетрафенилборат железа $Fe(C_{10}H_{13})_2[B(C_6H_5)_4]_2$	49	9
19 Дитетрагидроинденилрейнекат железа $Fe(C_{10}H_{13})_2[Cr(SCN)_4(NH_3)_2]_2$	44	4
20 Циклопентадиенилтрикарбонилмарганец $Mn(C_5H_5)(CO)_3$	64	19
21 Метилциклопентадиенилтрикарбонилмарганец $Mn(C_5H_4CH_3)(CO)_3$	61	19
22 Диксилолхром $Cr(C_8H_{10})_2$	45	0
23 Бензолтрикарбонил хрома $Cr(C_6H_6)(CO)_3$	40	0
24 Гексакарбонил молибдена $Mo(CO)_6$	40	[illegible]
25 Толуолтрикарбонил молибдена $Mo(C_6H_5CH_3)(CO)_3$	35	−8
26 Циклопентадиенилтрикарбонилгидрид молибдена $MoH(C_5H_5)(CO)_3$	41	−2
27 Циклопентадиенилтрикарбонилгидрид вольфрама $WH(C_5H_5)(CO)_3$	41	−2
28 Циклопентадиенилтетракарбонил ванадия $V(C_5H_5)(CO)_4$	35	−8
29 Бензолтетракарбонил ванадия $V(C_6H_6)(CO)_4$	37	−5
30 Дициклопентадиенилдихлорид титана $Ti(C_5H_5)_2Cl_2$	92	0
31 Диметилциклопентадиенилдихлорид титана $Ti(C_5H_4CH_3)_2Cl_2$	92	0

KEY:
1 -- Compound
2 -- ONRM with the compound added
3 -- Δ ON
4 -- Dicyclopentadienyl nickel (nickelocene)
5 -- Dicyclopentadienylcarbonyl nickel
6 -- Tricyclopentadienyldicarbonyl nickel
7 -- Nickel acetylacetonate
8 -- Cobalt acetylacetonate
9 -- Iron acetylacetonate
10 -- Iron pentacarbonyl
11 -- Dicylcopentadienyl iron (ferrocene)
12 -- Dimethylferrocene /continued on following page/

/KEY to Table 45 on preceding page/:

13 -- Tetracyclopentadienyldicarbonyl iron
14 -- Diacetylferrocene
15 -- Dixylolreinicate iron
16 -- Dixyloltetraphenylborate iron
17 -- Dimesitylenetetraphenylborate iron
18 -- Ditetralintetraphenylborate iron
19 -- Dietetralinereinecate iron
20 -- Cyclopentadienyltricarbonyl manganese
21 -- Methylcyclopentadienyltricarbonyl manganese
22 -- Dixylol chromium
23 -- Benzenetricarbonyl chromium
24 -- Hexacarbonyl molybdenum
25 -- Toluenetricarbonyl molybdenum
26 -- Cyclopentadienyltricarbonylhydride molybdenum
27 -- Cyclopentadienyltricarbonylhydride tungsten
28 -- Cyclopentadienyltetracarbonyl vanadium
29 -- Benzenetetracarbonyl vanadium
30 -- Dicyclopentadienyldichloride titanium
31 -- Dimethylcyclopentadienyldichloride titanium

liquid with a grassy odor, boiling point 233° C, specific gravity 1.3884 g/cm^3, and a pour point 1.5° C. MCTM is easily soluble in gasoline and is virtually insoluble in water (0.007 percent by weight at 25° C).

The antiknock effectiveness of MCTM was studied in commercial gasolines and in individual hydrocarbons [87]. A test made in individual hydrocarbons [71] showed that the hydrocarbons which have the highest sensitivity to TEL also disclose the greatest response to MCTM (Fig. 55). Among the hydrocarbons tested, the greatest response to both TEL and MCTM is shown by normal-structure heptane, 2,2-dimethylbutane, and 2-methylpentane [56]. Naphthenic hydrocarbons have a somewhat lower response to MCTM than paraffinic, but exceed aromatic hydrocarbons somewhat in this indicator. The effectiveness of MCTM in olefins depends to a large extent on their structure. The response of octene-1 to manganese antiknock proved to be 14 times greater than the response of diisobutylenes [71].

When a test was made of the comparative effectiveness of MCTM and TEL using an artificial mixture consisting of 40 percent toluene, 30 percent heptane, 20 percent diisobutylene, and 10 percent isooctane (TD-3 fuel), it was found that MCTM is twice as effective as TEL when the octane number was determined by the Research Method, and is equivalent to TEL for a rating based on the Motor Method.

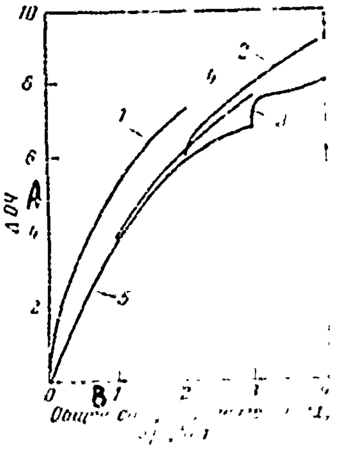


Fig. 56. Rise in the octane number of gasoline upon the addition of MCTM and TEL /16, 80, 81, 84/:
1 -- MCTM
2 -- blend of TEL and MCTM (2:1)
3 -- blend of TEL and MCTM (3:1)
4 -- blend of TEL and MCTM (1:1)
5 -- TEL

KEY: A -- ΔON
B -- Total metal content, g/3.78 liter

The response of gasolines to MCTM depends on their chemical composition. Gasolines which have the higher response to TEL as a rule show an even greater response to MCTM. The content in gasolines of paraffinic and aromatic hydrocarbons has the principal effect on gasoline response to MCTM. As the content of paraffinic hydrocarbons is increased, and as the content of aromatic hydrocarbons is reduced, gasoline response to CTM rises. Alkylates, natural gasolines, and C_5 -- C_6 hydrocarbons of branched structure have high response to MCTM.

Based on a test made of 41 samples of various commercial gasolines in the United States, it was found that MCTM on the average is twice as effective as TEL (on a metal basis) when antiknock properties are determined by the Research Method [15]. For ratings by the Motor Method, the antiknock effectiveness of MCTM and TEL is approximately the same.

In tests made of the manganese antiknock, a typical feature was noted: it enhances the knock resistance of gasoline containing TEL; here the first portions of MCTM added are especially effective [75, 80, 81, 84]. The same amount of CTM increases the octane number of ethyl gasoline more than non-ethyl gasoline: the higher the TEL content in a gasoline, the greater the effect resulting from adding MCTM [16] (Fig. 56). This phenomenon of the promoting action of MCTM on the antiknock effectiveness of TEL made it possible to formulate the problem of the combined use of these antiknocks. An antiknock blend AK-33 Mix, consisting of TEL and MCTM (0.052 g of manganese per ml TEL) was produced in the United States [80, 81]. Interestingly, the promoting action on TEL is exerted not only by the MCTM, but also by several other manganese compounds [16].

Studies made of the antiknock effectiveness of MCTM in engines in stand and operating conditions showed a considerably greater effectiveness for this antiknock than could be anticipated from the results of determining octane number by the Research and, especially, by the Motor methods [74, 82].

In tests made on a single-cylinder engine, it was found that the knock resistance of gasoline containing MCTM is 3-4 octane points higher than for the determination of octane number by the Research Method [74].

Numerous road tests in modern vehicles revealed that the knock resistance of gasolines containing MCTM in service conditions corresponds more fully into the octane number found by the Research Method than by the Motor Method (Table 46).

No special studies on the mechanism of the antiknock action of manganese antiknocks have been published in foreign literature. Based on the investigations and tests that have been conducted, it was hypothesized [16] that the mechanism of MCTM action evidently is the same as for TEL. It is assumed that initially MCTM decomposes and forms a metal or oxides of metal in the finely dispersed state. Active oxide compounds of manganese probably are also the compounds which break the chain reactions leading to detonation. Obviously, manganese antiknock decomposes the same active compounds as does TEL. In favor of this assumption is the degree of identity in response shown by commcrical fuels and pure hydrocarbons to MCTM and TEL.

The exceptionally high effect of MCTM when added in small amounts to strongly ethyl gasolines (promoting the effect) can be accounted for [71] by the change in the surface area of the particles of lead oxides that are formed. When particle size is reduced, the overall surface area of the particles is increased and, therefore, so is the catalytic action and the antiknock effect. A more exact explanation of the promoting effect awaits further investigation.

Extended stand and road tests were made of automotive gasolines to find what effect gasolines containing antiknocks have on the reliability and longevity of engine operation. In the tests, the criterion of the rating of engine service life included the duration of operation of exhaust valves and spark plugs, and also the total engine wear and the corrosion of its main parts.

Table 46. Effectiveness of TEL and MCTM When Added Together to Various Gasolines /16/

ТЭС, мл/л 1	МЦТМ, г/л 2	ОЧИМ 3	ОЧММ 4	ОЧДМ при n, об/мин 5				
				1500	2000	2500	3000	Средние 6
				7 Бензин А				
0	0	90,7	73,5	90,1	89,6	90,8	89,9	90,1
0	0,066	94,4	82,4	93,2	93,5	93,8	92,2	93,2
0	0,132	95,7	83,5	94,5	95,0	94,1	93,2	94,2
0	0,264	97,3	83,7	95,5	96,5	95,9	94,9	95,7
0	0,528	99,2	85,0	97,4	98,9	97,6	96,8	97,5
0,792	0	98,0	85,2	96,0	96,8	96,2	95,0	96,0
0,792	0,026	98,8	86,0	94,9	97,6	97,4	96,5	97,0
0,792	0,066	98,9	86,2	96,6	97,6	97,3	96,5	97,0
0,792	0,132	99,4	86,5	97,3	97,7	97,6	96,8	97,3
0,792	0,264	100,0	87,0	97,3	97,9	97,6	96,7	97,4
				8 Бензин Б				
0	0	90,6	83,0	88,5	89,6	89,9	89,7	89,4
0	0,066	94,1	84,6	89,8	92,5	93,7	93,3	92,3
0	0,132	95,7	85,3	92,9	94,2	95,4	94,5	94,3
0	0,264	97,7	86,5	94,8	96,4	97,8	97,0	96,5
0	0,528	99,6	88,2	97,0	98,9	99,4	99,0	98,6
0,792	0	99,0	90,7	97,1	99,1	99,4	99,5	98,8
0,792	0,026	99,3	90,6	96,4	99,0	[illegible]	99,7	98,8
0,792	0,066	99,5	91,0	97,5	99,9	100,6	100,4	99,9
0,792	0,132	99,7	91,0	98,8	99,4	99,4	99,8	99,1
0,792	0,264	100,8	91,4	97,9	100,0	100,8	99,9	99,7
				9 Бензин В				
0	0	91,0	80,4	90,0	91,1	92,1	91,2	91,2
0	0,066	94,7	82,8	[illegible]	93,5	94,2	92,6	93,4
0	0,132	95,2	83,7	94,5	95,8	96,6	94,7	95,2
0	0,264	97,5	84,9	97,6	97,1	97,5	[illegible]	96,7
0	0,528	99,4	85,9	98,4	99,2	98,9	97,8	98,6
0,792	0	98,7	88,5	[illegible]	98,5	98,7	98,0	98,1
0,792	0,026	100,1	88,4	97,6	99,6	99,2	98,4	98,7
0,792	0,066	100,5	[illegible]	[illegible]	99,8	99,4	98,8	99,1
0,792	0,132	100,7	88,8	98,1	99,2	99,5	98,6	98,9
0,792	0,264	[illegible]	[illegible]	98,1	99,8	99,4	98,8	99,1

KEY: 1 -- TEL, ml/l
2 -- MCTM, g/l
3 -- ONRM
4 -- ONMM
5 -- ONR for n, rpm, as indicated
6 -- Mean
7 -- Gasoline A
8 -- Gasoline B
9 -- Gasoline C

The tests showed that the service life of exhaust valves is determined by the presence of TEL in a gasoline and by the MCTM concentration. When TEL is absent, MCTM has only a slight effect on the performance of the exhaust valves. The required service life of valves in this case is achieved without adding additional additives [83]. When small amounts of MCTM are added to a gasoline containing TEL, the service life of engine exhaust valves is severely reduced, but on the other hand with increase in the MCTM concentration this service life will rise to the same value as when MCTM is absent. This phenomenon, established in various engines during their operation, has thus far not been explained.

The problem of extending the service life of exhaust valves by adding small amounts of MCTM to ethyl gasoline is readily solved by adding several phosphorus compounds to the gasoline. When added in the amount of 0.3-0.4 of the theoretically required quantity to convert all the manganese into orthophosphate, phosphorus eliminates the premature breakdown of exhaust valves [83].

The service life of engine spark plugs, when ethyl gasolines containing MCTM are used, depends on the vehicle operating conditions: at low loads it sharply rises, while at high loads it is reduced. The operation of spark plugs is disrupted mainly due to electrode short-circuiting. No reports on any additives that extend the service life of spark plugs in severe operating conditions have been published in the literature.

When MCTM is used as an independent antiknock, spark plug service life is reduced less abruptly at high loads, in spite of the fact that even in this case electrode short-circuiting can occur. The operation of spark plugs when gasolines containing only MCTM are used is disrupted later and at higher MCTM concentrations than when ethyl gasolines containing MCTM are employed [83].

Tests showed that adding MCTM to gasolines does not increase wear and does not affect engine corrosion. A decrease in wear for operation on gasolines containing MCTM (without TEL) was noted even in operating an unwarmed engine, that is, in conditions favorable to corrosion. The effect of gasolines containing MCTM on deposit formation and on the requirements engines impose on fuel knock resistance was investigated in conditions of the experimental operation of a park of passenger cars for a total run of more than 1.6 million km [16].

Gasolines containing MCTM and TEL together, from the standpoint of deposit formation, differ only slightly from ethyl gasolines. Adding MCTM to ethyl gasoline somewhat increases the number of premature firings and glow ignition cases. Phosphorus compounds eliminate these phenomena.

When gasolines containing MCTM but no TEL were used in an engine, deposit formation was very slight, and premature ignition almost never occurred. The engine requirements on fuel knock resistance after the engine has been operated on a gasoline containing MCTM proved to be significantly lower than after the same run using ethyl gasoline [83]. In the studies it was stressed that the absence of glow ignition when an engine was operated on gasoline containing MCTM and phosphorus will take on growing importance with an increase in the compression ratio of modern engines and the rise in the octane number of automotive gasölines [86].

The prospects of using manganese antiknock are closely bound up with their production costs. Based on rough calculations, the cost of MCTM is roughly 4 times higher than the cost of TEL (calculated for the same weight of metal in the antiknocks). Since for the same metal concentration in a gasoline, MCTM is twice as effective as TEL, obviously the increase in the octane number of gasoline if MCTM is added will cost twice as much as if TEL is added. The view has been advanced that from economic considerations manganese antiknocks can compete with TEL only if their costs will be considerably reduced.

Ethyl Corporation specialists maintain that the increased effectiveness of small portions of MCTM must be used now by adding them to strongly ethyl gasolines (the phenomenon of the promoting effect of MCTM on TEL effectiveness). They present the following example. The octane number of one of the fuels containing 0.8 ml/l of TEL, upon the addition of 0.08 g/l of manganese, was raised to 99.7. To achieve this same octane number using only TEL required adding 0.52 g/l of lead. In this case 0.08 g of manganese was found to be equivalent to 0.52 g of lead. In other words, the effectiveness of the manganese antiknock in these conditions is 6.5 times greater than TEL effectiveness. Naturally, here the use of MCTM is economically justified even if its cause exceeds TEL cost by a factor of 4.

Based on the above considerations, at the present time in other companies it is deemed advisable to use the manganese antiknock only as an additive to TEL. The use of manganese compounds as an independent antiknock is suggested only after their costs have been lowered.

In the USSR the main trend in research on manganese antiknock consists of studying the conditions and characteristics of its use in pure form without TEL — to eliminate the high toxicity of ethyl gasolines [3, 20, 28, 32, 78-105].

The synthesis of manganese compounds of sandwich structure was achieved for the first time in our country by A. N. Nesmeyanov, K. N. Anisimov, and V. A. Zaytsev.

At the present time a single method for the primary selection and establishing of the comparative effectiveness of antiknocks has been proposed [102]. The effectiveness is estimated in two blends of hydrocarbons in pure form, differing in sensitivity, and in the presence of an organic sulfur compound, which at once permits rating also the antagonistic effects. The effectiveness of the antiknock is compared with TEL based on a previously plotted reference standard curve and is expressed in percentages.

The results of rating several compounds by this procedure (Table 47) shows that the relative effectiveness of manganese antiknocks depends on the composition of mixtures, as well as on the method of octane number determination.

In the presence of aromatic and unsaturated hydrocarbons, the relative effectiveness of manganese antiknocks is reduced.

Based on the Research Method of octane number determination, the effectiveness of manganese antiknocks is rated higher than by the Motor Method. The relative rating of manganese antiknocks rises by a factor of 2.5 during the transition from a comparison made at identical additive concentrations to a comparison made at identical metal concentrations.

In the presence of organic sulfur compounds, the effectiveness of manganese antiknocks decreases to a lesser extent than tetraethyl lead effectiveness. This very important fact makes it possible to explain the fluctuations in the relative rating of manganese antiknocks and the TEL in commercial gasolines.

Decacarbonyl manganese, several derivatives of CTM, and ferrocene proved to be less effective antiknocks.

A study of the effectiveness of manganese antiknocks when added to gasolines of various origins truly confirmed the findings of the preliminary rating (Table 48).

CTM in A-66 gasoline consisting mainly of paraffinic and olefinic hydrocarbons proved to be more effective than TEL. Both antiknocks (CTM and TEL) showed roughly the same effectiveness in A-72 gasolines. The effectiveness of CTM in catalytic cracking and especially reforming gasolines is lower than that of TEL. On the average, one must obviously assume that the effectiveness of CTM and TEL when added to commercial automotive gasolines is about the same (for identical concentrations based on the weight of antiknocks as a whole). If one determines the effectiveness of antiknocks at identical metal concentrations, manganese antiknocks prove to be much more effective than TEL.

An American sample of antiknock (MCTM) and domestic manganese antiknock (CTM) revealed a virtually identical effectiveness in the most varied gasolines (Table 48). A similar effect was also obtained in the primary rating of these compounds (Table 47).

With increase in CTM concentration in gasolines, its effectiveness diminishes; here the trend of the change in octane numbers as a function of antiknock concentration is roughly the same for both CTM and TEL (Fig. 57). Adding CTM to gasolines eliminates their sensitivity to a somewhat greater effect than adding TEL at the same concentration. The effectiveness of CTM was rated not only by laboratory methods, but also in a full-sized engine -- on straight-run gasoline (Table 49).

Table 47. Rating of Effectiveness of Various Antiknocks

Показатель 1	ЦТМ 2	МЦТМ 3	ДКМ 4	5 Продукты алкилирования ЦТМ		Ферроцен 8
				фракцией полимербензина 6	узкой фракцией изооктиленов 7	
Содержание металла, % 9	27,0	25,2	28,0	11,7	13,8	30,0
10 Смесь из 60% изооктана и 40% гептана						
ОЧММ 11						
без S 12	72,6	72,7	71,6	66,6	67,0	69,4
с 0,05% S 12a	72,1	71,8	69,7	66,4	66,7	69,4
Относительная эффективность * 19						
12 Без S						
при одинаковой концентрации присадок 13	48	49	42	22	24	32
при одинаковой концентрации металлов 14	113	124	95	120	109	70
С 0,05% S 12a						
при одинаковой концентрации присадок 13	75	72	57	34	35	53
при одинаковой концентрации металлов 14	175	181	130	188	160	110
15 Смесь из 10% толуола, 30% гептана, 20% диизобутилена и 10% изооктана						
ОЧИМ 16	95,1	95,0	93,5	92,8	92,7	93,2
ОЧММ 11	82,2	81,9	80,8	79,9	80,0	80,2
Относительная эффективность * 19						
По моторному методу 17						
при одинаковой концентрации присадок 13	31	29	20	12	13	11
при одинаковой концентрации металлов 14	75	76	47	70	60	30
По исследовательскому методу 18						
при одинаковой концентрации присадок 13	62	60	40	34	33	38
при одинаковой концентрации металлов 14	145	151	95	188	159	80

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* The effectiveness of TEL is taken as 100 percent.
/KEY given on following page/

/KEY to Table 47 on preceding page/

1 -- Indicator
2 -- CTM
3 -- MCTM
4 -- DCM
5 -- Products of the alkylation of CTM
6 -- using polymer gasoline fraction
7 -- using narrow fraction of isooctylenes
8 -- Ferrocene
9 -- Metal content
10 -- Blend of 60 percent isooctane and 40 percent heptane
11 -- ONMM
12 -- not containing sulfur
12a -- containing 0.05 percent S
13 -- for the same concentration of additives
14 -- for the same concentration of metals
15 -- Blend of 40 percent toluene, 30 percent heptane, 20 percent diisobutylene, and 10 percent isooctane
16 -- ONRM
17 -- Based on the Motor Method
18 -- Based on the Research Method
19 -- Relative effectiveness *

The relative rating of CTM effectiveness in a full-sized engine is higher than when tested by standard methods of octane number determination on IT-9 stands. The difference between the actual octane numbers of gasolines containing TEL and CTM decreases steadily with increase in rpm (cf. Table 49). At low engine crankshaft rpm, the antiknock rating of a gasoline without antiknocks and of a gasoline containing CTM decreases markedly, while for a gasoline containing TEL it remains roughly constant. Both antiknocks at low rpm showed higher effectiveness in increasing actual octane numbers than at high rpm.

Data on a preliminary rating (cf. Table 47) showed that the antagonistic action of organic sulfur compounds on CTM effectiveness is much less than on TEL effectiveness. These results were fully confirmed in laboratory studies and stand tests (Fig. 58). It was found that the antagonistic action of organic sulfur compounds toward CTM proved to be somewhat less than toward TEL. In the absence of sulfur compounds, the actual knock resistance of gasoline containing TEL (0.84 g/kg) in all engine operating regimes is higher than the knock resistance of the same gasoline containing CTM in the same concentration. However, in the presence of organic sulfur compounds at a relatively low concentration (0.05 percent S), the situation changes sharply. CTM-containing gasoline showed higher antiknock properties in all engine operating regimes than TEL-containing gasoline (cf. Fig. 58).

Table 48. Response of Gasolines to Antiknocks (1 g of antiknock per 1 kg of fuel)

Бензин 1	ОЧ топлива 2				
	чистого 3	с ТЭС 4	с ЦТМ 5	с МЦТМ 6	с ДКМ 7.
Моторный метод 8					
Бензин А-66 9	59,4	70,0	71,2	71,0	68,2
Бензин А-72 10	72,3	78,2	78,4	78,2	76,6
Компонент прямой перегонки 11	49,4	63,5	61,8	65,0	61,7
Компонент термического крекинга 12	66,0	71,7	72,4	72,0	70,7
Компонент каталитического крекинга 13	73,0	79,8	79,0	79,0	77,6
Компонент каталитического риформинга 14	72,6	81,3	78,1	78,0	75,9
Исследовательский метод 15					
Бензин А-66 9	60,5	72,0	73,2	73,0	68,9
Бензин А-72 10	77,6	86,6	87,5	87,7	85,6
Компонент каталитического крекинга 13	78,0	86,1	85,0	85,6	83,0
Компонент каталитического риформинга 14	76,8	88,0	85,1	85,3	83,6

KEY:
1 -- Gasoline
2 -- ON of fuel
3 -- pure
4 -- containing TEL
5 -- containing CTM
6 -- containing MCTM
7 -- containing DCM
8 -- Motor Method
9 -- A-66 gasoline
10 -- A-72 gasoline
11 -- Straight-run component
12 -- Thermal cracking component
13 -- Catalytic cracking component
14 -- Catalytic reforming component
15 -- Research Method

The difference in the relative rating of TEL and CTM effectiveness based on laboratory methods and in a full-sized engine is a consequence of the dissimilar rating of TEL effectiveness by various methods. In the conditions of the Motor and Research methods of octane number determination, gasolines containing TEL showed higher knock resistance than when the actual octane numbers were determined in a full-sized engine. At the same time, for gasolines containing CTM, ratings of knock resistance by laboratory methods were very close to ratings of actual knock resistance in a full-sized engine (Table 50).

The lower rating of the knock resistance of gasolines containing TEL in a full-sized engine, in addition to the high antagonistic effect of organic sulfur compounds toward TEL, is the reason for the change in the relative rating of TEL and of CTM in sulfur automotive gasolines.

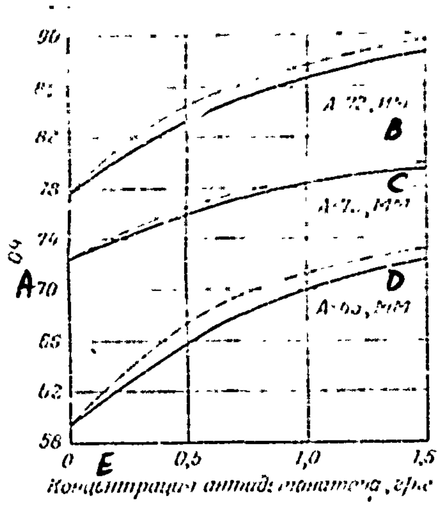


Fig. 57. Effect of concentration of antiknocks on the knock resistance of various gasolines:

_ _ _ _ _ CTM _______ TEL

KEY: A -- ON
B -- A-72 gasoline, RM
C -- A-72 gasoline, MM
D -- A-66 gasoline, MM
E -- Concentration of antiknock, g/kg

In the conditions of the growing use in our country of sulfur automotive gasolines, the property of CTM only slightly diminishing in effectiveness when exposed to organic sulfur compounds takes on particularly vital importance. One must bear in mind that the actual knock resistance of sulfur automotive gasolines containing CTM in engines roughly coincides with the rating based on laboratory octane numbers, while the antiknock properties of gasolines containing TEL in conditions of full-sized engines are significantly lower than in single-cylinder stands for octane number determination. The high antiknock properties are highly important, but not the only quality associated with the chemical composition of a compound tested as an antiknock additive for gasoline. This compound must satisfy general requirements imposed on automotive gasoline additives.

The main disadvantage of TEL, as already stated, is its high toxicity. A study of CTM showed that the "toxocity of gasoline solutions of CTM is caused by the toxicity of the gasolines" [100]; in other words, adding CTM in amounts up to 1.0 g/kg does not increase gasoline toxicity. This is the principal and decisive advantage of CTM compared with TEL.

Table 49. Increase in Actual Knock Resistance of Straight-run Gasoline Upon the Addition of Manganese Antiknock and Tetraethyl Lead (M-21A Engine)

Детонационная стойкость 1	Исходный бензин 2	с 0,82 г ТЭС/кг 3	с 0,82 г ЦТМ/кг 4
ОЧИМ 5	71,0	83,0	79,9
ОЧММ 6	69,2	81,2	78,0
ФОЧ 7			
1000 об/мин 8	65,3	80,0	77,0
1200 »	67,2	79,6	77,5
1400 »	68,9	79,5	78,0
1800 »	69,7	80,0	78,6
2200 »	68,9	79,2	78,2

KEY: 1 -- Knock resistance
2 -- Initial gasoline
3 -- containing 0.82 g TEL/kg
4 -- containing 0.82 g CTM/kg
5 -- ONRM
6 -- ONMM
7 -- AON
8 -- rpm

CTM at the concentrations used dissolves completely and rapidly in gasolines at ordinary temperatures, is insoluble in water, is not extractible from gasolines with water, and does not precipitate from gasoline solutions at low temperatures [94].

The corrosiveness and chemical stability of gasolines containing CTM is approximately the same as for gasolines containing TEL. The acidity of gasolines after the addition of CTM remains unchanged. The content of existent gums in gasoline containing CTM proves to be overstated by 2-4 mg/100 ml, that is, just as in gasoline containing TEL.

A heavy floclike precipitate containing more than 30 percent manganese is formed very rapidly in gasolines containing CTM upon exposure to sunlight. An effective means of protecting gasoline solutions of CTM against the action of sunlight is the addition of dyes to them. In this case, the antiknock additive based on CTM can incorporate a dye in its composition.

An important indicator of the quality of the antiknock is its effect on the formation of deposits in the intake system and the formation of carbon deposits in the combustion chamber. The tendency of gasolines containing antiknocks to form deposits in the intake line is rated with a single-cylinder engine by the increment in the weight of a removable metal strip inserted in the intake line. The tendency of gasolines to form carbon deposits is rated by the weight increment of a special carbon deposit-induc

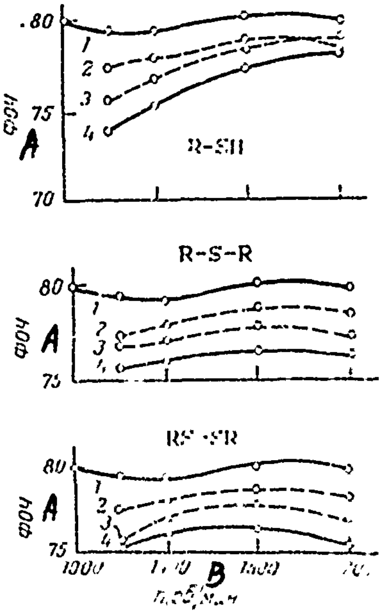


Fig. 58. Effect of mercaptans, sulfides, and disulfides on the actual knock resistance of gasoline containing antiknocks (amount of antiknocks in all cases was 0.84 g/kg):

1 -- gasoline + TEL
2 -- gasoline + CTM
3 -- gasoline + CTM + 0.05 percent S
4 -- gasoline + TEL + 0.05 percent S

KEY: A -- AON
B -- n, rpm

deposits is rated by the weight increment of a special carbon deposit-inducer installed in the combustion chamber of a single-cylinder engine or a full-sized automotive engine.

The effect of antiknocks on carbon deposit formation and the amount of deposits in an intake system are illustrated by the following data [96]:

Table 50. Effect of Organic Sulfur Compounds (0.05 percent S) on the Antiknock Properties of Gasoline Containing CTM (0.84 g/kg)

Детонационная стойкость 1	ОЧ 2	ΔОЧ 3
Бензин Б-70 + меркаптаны 4		
ИМ 5	78,8	—1,1
ММ 6	77,2	—0,8
На двигателе М-21А 7		
1200 *об/мин* 8	75,5	—1,8
1400 »	76,8	—2,1
1800 »	78,6	—0.2
2200 »	78,3	0,0
Бензин Б-70 + сульфиды 9		
ИМ 5	78,6	—1,3
ММ 6	77,6	—0,4
На двигателе М-21А 7		
1200 *об/мин* 8	76,5	—0,8
1400 »	77,0	—1,9
1800 »	77,8	—1,0
2200 »	77,0	—1,3
Бензин Б-70 + дисульфиды 10		
ИМ 5	78,2	—1,7
ММ 6	76,8	—1,2
На двигателе М-21А 7		
1200 *об/мин* 8	75,5	—1,8
1400 »	77,0	—1,9
1800 »	78,0	—0,8
2200 »	77,0	—1,3

KEY: 1 -- Knock resistance
2 -- ON
3 -- Δ ON
4 -- B-70 gasoline + mercaptans
5 -- RM
6 -- MM
7 -- In the M-21A engine
8 -- rpm
9 -- B-70 gasoline + sulfides
10 -- B-70 gasoline + disulfides

	Carbon deposit formation, mg/hr	Deposits on a strip in the intake system, mg/hr
A-66 gasoline	26	25
As above + 0.82 g/kg TEL	42	41
As above + 0.80 g/kg CTM	31	32

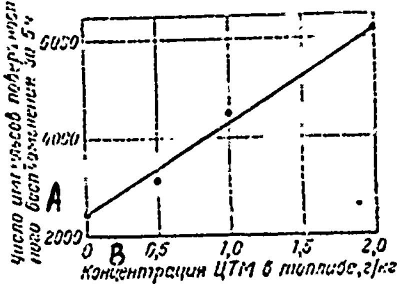


Fig. 59. Effect of CTM concentration on the surface ignition in an engine /96/

KEY: A -- Number of surface ignition firings in 5 hours
B -- Concentration of CTM in fuel, g/kg

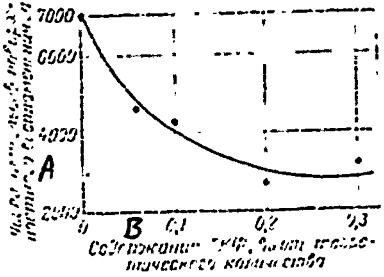


Fig. 60. Effect of the concentration of phosphorus additive on surface ignition in an engine /96/

KEY: A -- Number of surface ignition firings in 5 hours
B -- Content of TCP, percent of theoretical amount

These results show that when an engine is operated on gasoline containing CTM less deposits are formed in the intake system and in the combustion chambers than when gasoline containing TEL is used. With increase in the concentration of organometallic antiknocks, the tendency of a gasoline to form carbon deposits rises, however at all concentrations CTM produces less carbon deposit formation than TEL.

Carbon deposits forming upon the combustion of gasoline containing CTM differ externally from ordinary carbon deposits: they have a characteristic porous structure, readily separate from the walls of the deposit inducer, and have a gray color with a yellowish tinge.

When an engine is operated on gasoline containing CTM, two characteristic features of the carbon deposits formed are noted. The first feature is that this kind of carbon deposit causes pre-ignition of the working mixture produced by glowing particles. The frequency of glowing ignition is virtually directly proportional to the CTM concentration in the gasolines. (Fig. 59). The addition of phosphorus compounds (tricresylphosphate) effectively lowers the frequency of glowing ignition (Fig. 60). Here the optimal concentration of tricresylphosphate is 0.2 of the theoretically required amount to convert the manganese contained in gasoline to orthophosphate (about 0.16 ml tricresylphosphate per kg of gasoline, when it contains 0.8 g/kg of CTM).

A second feature of deposits remaining in an engine after the combustion of gasolines containing CTM is that they cause misfirings of the spark plugs.

When an engine is operated on gasolines containing CTM, the carbon deposits formed on the insulators of the spark plugs are a current conductor at high temperatures and cause current leakage along the surface of the insulator (shunting action of carbon deposits). Additionally, the formation of slender current-conducting filaments between electrodes has been observed, causing short-circuiting of the electrodes (bridge formation). Deposits of carbon on electrodes shorten the interelectrode gap and degrade the conditions of spark discharge formation.

In extended tests of a full-sized engine on a stand, it was found that on gasoline containing 0.8 g/kg of CTM, spark plugs can operate for only about 29 hours without being cleaned free of carbon deposits. Naturally, this operating time is unsuitable for the service conditions of automotive transportation. Adding a scavenger to the manganese antiknock composition -- -- ethyl bromide (to remove manganese combustion products) -- permits an extension of the service time of spark plugs without cleaning on the average to 60-70 hours [101]. An even better effect is achieved by adding to CTM a compound such as bis-ethylxanthogen ($C_6H_{10}O_2S_4$), When it is present, the operating time of spark plugs without cleaning rises to 89 hours. It must be noted that the improvement in spark plug functioning upon the addition of ethyl bromide and bis-ethylxanthogen was not a consequence of the significant reduction of carbon deposit formation (Table 51).

The amount of carbon deposits upon the addition of scavengers is only slightly reduced; therefore, the action of these additives is not associated so much with the removal of manganese compounds as with their "transformation". Obviously, future effective additives to the manganese antiknock must be called not "scavengers", but "transformers" of carbon deposits. Efforts to find these compounds are underway at the present time. But what does this transformation of carbon deposits amount to, which is so necessary when an engine is being operated on a gasoline containing CTM?

Studies showed that the shunting resistance of a spark plug operating on gasoline containing CTM is less than for a new spark plug or for one that is operating on gasoline containing no antiknock [92] (Fig. 61). The difference in the spark plug resistances at high temperatures is particularly great.

Several spark plugs with carbon deposits that had functioned in an engine with misfiring were tested in a special instrument of the NAMI. The spark plugs proved fully serviceable at temperatures to 500-530° C; when heated above 530° C the spark plugs began to operate with misfirings, and ceased functioning at all at 700° C. With a further decrease in temperature, spark plug serviceability was restored.

Table 51. Amount of Deposits Formed in Engines in 400 Hours of Testing When Operating on Gasolines Containing Various Antiknocks

Бензин 1	Количество нагара, г 2				
	на днище поршня 3	на головке цилиндра 4	на выпускном клапане 5	на впускном клапане 6	всего 7
8 Бензин А-66 + 0,82 г ТЭС на 1 кг с выносителем (бромистым этилом)*	5,65	6,00	5,65	2,50	19,80
9 То же + 0,8 г ЦТМ на 1 кг без выносителя	3,40	7,20	0,40	0,40	11,40
10 То же + 0,8 г ЦТМ на 1 кг с выносителем (бромистым этилом)	4,38	4,84	1,62	0,41	11,25
11 То же + 0,8 г ЦТМ на 1 кг с бисэтилксантогеном	4,84	4,45	0,39	0,35	10,03

---

* Tests were conducted over a period of 330 hours.

KEY: 1 -- Gasoline
2 -- Amount of deposits, g
3 -- on piston head
4 -- on cylinder head
5 -- on exhaust valve
6 -- on intake valve
7 -- total
8 -- A-66 gasoline + 0.82 g TEL per kg, containing scavenger (ethyl bromide) *
9 -- As above + 0.8 g CTM per kg, not containing scavenger
10 -- As above + 0.8 g CTM per kg, containing scavenger (ethyl bromide)
11 -- As above + 0.8 g CTM per kg, containing bis-ethylxanthogen

These results suggest that the combustion products of CTM have high electroconductivity, rising sharply with temperature. Unfortunately, no direct determinations of this indicator have been made yet for various oxide compounds of manganese. These data obviously are necessary in efforts to find new additives to manganese antiknock. The additives must contain elements that would, without affecting the antiknock properties of CTM, combine its decomposition products into compounds with low electroconductivity at eleveated temperatures.

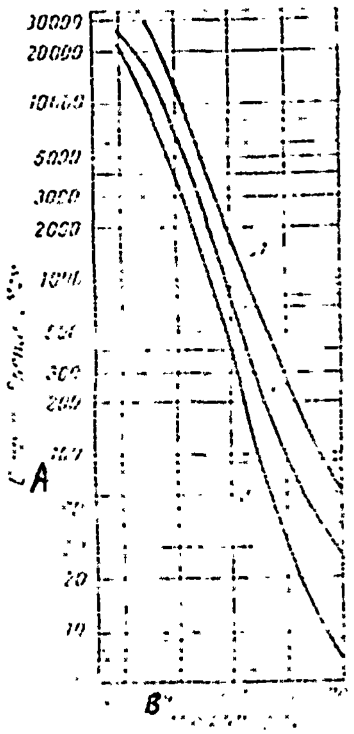


Fig. 61. Dependence of shunting resistance of spark plugs on temperature:

1 -- new spark plugs
2 -- spark plugs operating with gasoline not containing antiknock
3 -- spark plugs operating with gasoline containing CTM

KEY: A -- Resistance, megaohms
B -- Temperature, °C

At the present time, domestic motor vehicles of various grades have been run for more than 6 million km on gasolines containing manganese antiknock. During all these tests it was shown that adding CTM to gasolines does not cause an increase in the wear on engine parts [93, 98]. Wear determined by the methods of cut-out crescents, micrometry, and weighing of parts proved to be less than wear resulting from similar tests of ethyl gasolines and even gasolines containing no antiknocks.

It was established that using gasolines containing CTM does not cause a deterioration in the technical condition of engines. The only drawback of gasolines containing CTM is the accelerated malfunctioning of spark plugs, which is accompanied by misfirings in the performance of several engine cylinders.

Tests showed that owing to the accumulation of carbon deposits when an engine is operated on gasoline containing CTM in an amount not higher than 0.5 g/kg, it was found necessary to regularly clean spark plugs every 16,000 km in the sand-jet instrument of the GARO [Trust for the Manufacture of Garage Equipment] [92]. However, even sand-jet cleaning does not ensure the complete restoration of spark plug efficiency [93].

At the present time work on the investigation and introduction of manganese antiknock is continuing in efforts to find additives that transform carbon deposits, to improve spark plug design, to use new materials for insulators and electrodes of spark plugs, to develop special coatings, and so on.

Use of Ethyl Gasolines

Tetraethyl lead in the pure form has not been successfully used as an antiknock additive to gasolines, since its combustion products deposit out and accumulate on the walls of combustion chambers as carbon deposits, and after a short time the engine ceases to operate.

The main combustion product of TEL -- lead oxide -- has a high melting point (880° C), therefore it deposits on the relatively colder parts of an engine as a hard gray coating.

It has been calculated that if all the lead remained in the engine, the combustion chambers would be entirely filled with lead and its compounds after only 40 hours of operation. Actually, not all the lead compounds remain in the engine; most of them due to the high exhaust flow rates of gases from the cylinders are swept up by the flow and carried out of the engine. Experiments show that about 90 percent of the total amount of lead introduced with the gasoline is swept out of combustion chambers with the spent gases. But even the remaining 10 percent of lead compounds produces deposits that are so heavy that they cause serious malfunctions in engine operation.

Tetraethyl lead is added to gasoline in a mixture with substances capable, upon combustion, of forming with the lead or its oxides compounds that have higher saturated vapor pressures and lower melting points. These compounds have been called scavengers, and the blend of TEL with the scavengers is called ethyl fluid.

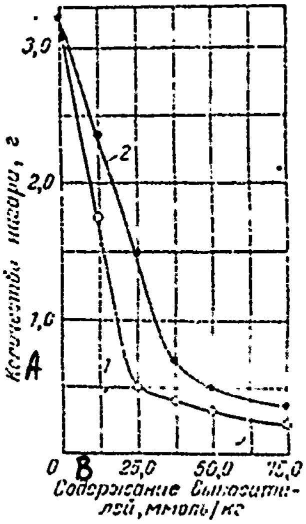


Fig. 62. Effect of scavenger concentration on deposit formation /106/:
1 -- dibromoethane
2 -- dichloroethane

KEY: A -- Amount of deposit, g
B -- Content of scavenger, mmole/kg

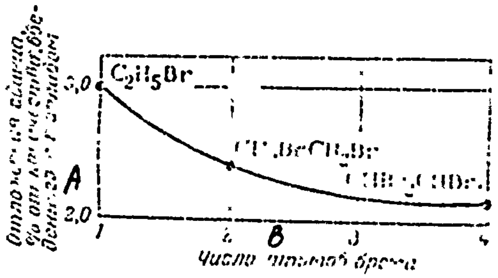


Fig. 63. Effect of extent of bromine substitution of hydrogen atoms in scavenger molecule on lead deposits in engine combustion chamber /106/

KEY: A -- Lead deposits in percent of amount introduced with fuel
B -- Number of bromine atoms

Organic halogen compounds are used as scavengers, decomposing at high temperatures to form hydrohalogenide acid and the corresponding hydrocarbon. Ethyl bromide decomposes according to the following scheme:

$$C_2H_5Br \longrightarrow C_2H_4 + HBr$$

The hydrohalogenide formed reacts with the lead decomposition and oxidation products, forming halogenide compounds of lead:

$$PbO + 2HBr \longrightarrow PbBr_2 + H_2O$$
$$Pb + 2HBr \longrightarrow PbBr_2 + H_2$$

Halogenide compounds of lead, having lower melting points, do not condense on engine parts and are swept out of the engine in the vapor state together with the exhaust gases. Scavengers containing bromine have gained widest acceptance, since their effectiveness proves to be higher than compounds containing chlorine (Fig. 62). The increase in the number of bromine atoms in the alkylbromide molecule increases its effectiveness as a scavenger (Fig. 63). However, only the halogenoalkyls containing not more than two halogen atoms per molecule have found practical use (Table 52).

The ratio of TEL to scavenger in ethyl fluids is selected so that the halogen can combine with all the lead (stoichiometric ratio) and there would be some (10–15 percent) scavenger reserve (Table 53).

Recently studies have been published showing the utility of using only bromide scavengers in ethyl fluids, which permit a significant increase in the longevity of automotive engines and a decrease in carbon deposit formation [107].

Earlier it was noted that the main advantage of organo lead compounds is their high effectiveness with an increase in the knock resistance of gasolines. Adding tetraethyl lead is the most advantageous method of raising the octane number of gasolines. However, the use of ethyl gasolines involves the following characteristics that must be reckoned with when operating engines.

1. Even in the presence of a scavenger, total removal of the TEL combustion products from an engine does not take place, therefore, when operating on ethyl gasoline increased carbon deposit formation is noted. As the TEL concentration in a gasoline is increased, the amount of the carbon deposits formed rises (Table 54).

The composition of deposits is determined by the temperature of the parts in the combustion chamber on which the deposits settle out. On hotter parts (exhaust valve and spark plugs), deposits contain 80–85 percent of the lead compounds; on the colder parts (piston, cylinder blockhead), the lead compounds in the deposits amount to 50–70 percent. The composition of lead deposits depends on the composition of the gasoline, quality of the scavenger, temperature conditions, and the like.

In the combustion of gasoline containing TEL, carbon deposits are formed containing lead oxide. In the presence of scavengers, the deposits contain, besides lead oxide, halogen compounds of lead and complex oxy-halogenide compounds of various compositions [109]:

	Melting Point, ° C
$PbBr_2$	370
$PbO \cdot PbBr_2$	497
$2PbO \cdot 3PbBr_2$	488 510
$2PbO \cdot PbBr_2$	710
$3PbO \cdot PbBr_2$	710
$6PbO \cdot PbBr_2$	740
PbO	888
$4PbO \cdot PbSO_4$	900–920
$2PbO \cdot PbSO_4$	[illegible]
$PbO \cdot PbSO_4$	[illegible]
$3Pb_3(PO_4)_2 \cdot PbBr_2$	[illegible]
$4PbO \cdot P_2O_5$	[illegible]
$Pb_3(PO_4)_2$	[illegible]

Table 52. Physical Properties of Lead Scavengers

Показатели 1	Бромистый этил 2	Дибромэтан 3	Дибромпропан 4	Хлористый этил 5	Дихлорэтан 6
ρ_4^{20}	1,460	2,182	1,933	0,8943	1,254
ν_{15}, *сст* 7	4,18	1,88	--	0,28	0,75
8 Температура кипения, °C	34,4	131,7	141,6	12.5	83,5
9 Температура плавления, °C	—119	+10	—56	—139	—35,5
10 Давление насыщенных паров при 20° C, *мм рт. ст.*	399	9	6	1044	145

KEY:
1 -- Indicators
2 -- Ethyl bromide
3 -- Dibromoethane
4 -- Dibromopropane
5 -- Ethyl chloride
6 -- Dichloroethane
7 -- centistokes
8 -- Boiling point
9 -- Melting point
10 -- Saturated vapor pressure, at 20° C, mm Hg

Upon combustion, sulfur ethyl gasolines produce deposits containing lead sulfate and complex compounds of the salts of lead with its oxide. It must be noted that the composition of deposits in combustion chambers is inconstant both with respect to engine operating time as well as thickness of deposits [110, 111]. Deposits have low thermal conductivity, therefore the temperature at the surface of deposits is always somewhat higher than at the metal surface. So as the layer of deposits increases in thickness, the temperature of its surface rises and the composition of the deposits changes (Fig. 64). And higher-melting compounds of lead accumulate in the upper layers of the deposits (Fig. 65).

Lead deposits are formed most intensively during the first hours of engine operation. With further engine operation on ethyl gasoline, less lead deposits are formed, but still the total amount of lead deposited steadily rises with time. And the rate of deposit formation in different parts of the combustion chamber varies.

The distribution of lead compounds in combustion chambers was investigated using radioactive isotopes [112]. An engine was operated for 100 hours on ordinary ethyl gasoline. Then to this ethyl gasoline was added a small amount of tetraethyl radium and the engine was run for 30 minutes on this mixture. After testing, the engine was dismantled and an x-ray film was applied to each part. In those place where radium was deposited the film was darkened. Thus, it was possible to show that the largest amounts of deposits form at the exhaust valve and the section of the combustion chamber adjoining it.

Table 53. Compositions of Ethyl Fluids (Percent by Weight)

Компоненты 1	Р-9 (СССР) 2	1-Т (СССР) 2	П-2 (СССР) 2	Автомобильная (СССР) 3	Q (Англия) 4	Автомобильная, фирмы «Октель» (Англия) 5	Тип I (ФРГ) 6	О-62 (США, Италия) 7
ТЭС 8	54,0	58,0	55,0	57,0	63,30	59,79	54,5	61,48
Бромистый этил 9	33,0	—	—	26,8	—	—	—	—
Дибромэтан 10	—	36,0	—	—	25,75	20,84	36,4	17,86
Дихлорэтан 11	—	—	—	13,9	8,72	18,30	—	18,81
Дибромпропан 12	—	—	34,4	—	—	—	—	—
Монохлорнафталин 13	6,8	—	5,5	—	—	—	9,0	—
Красящее вещество 14	0,1	0,5	0,1	2,3	0,10	1,07	0,1	2,65
Наполнитель 15	6,1	5,5	5,0		2,13		—	

KEY: 1 -- Components
2 -- (USSR)
3 -- Automotive (USSR)
4 -- (Great Britain)
5 -- Automotive, from Octel Company (Great Britain)
6 -- Type I (FRG)
7 -- 0-62 (United States, Italy)
8 -- TEL
9 -- Ethyl bromide
10 -- Dibromoethane
11 -- Dichloroethane
12 -- Dibromopropane
13 -- Monochloronaphthalene
14 -- Colorant
15 -- Filler

The increase in deposit formation from using ethyl gasolines causes greater engine requirements on the knock resistance of the fuels employed.

2. Deposits of lead compounds in a combustion chamber reduce the glow temperature of deposits, which is accompanied by the phenomenon of glowing ignition. This phenomenon was discussed in detail earlier, in the section on glowing ignition. For operation on ethyl gasoline, glowing ignition is eliminated by adding special additives containing phosphorus and boron.

3. The operating reliability of spark plugs depends on the composition of deposits formed on electrodes, insulators, and so on. Electrical resistance of a compound such as $PbBr_2$ is severely reduced even after relatively low temperatures (Fig. 66). The reduction of the electrical resistance of

Table 54. Effect of TEL on Deposit Formation in Engine /108/

Концентрация ТЭС в бензине, г/кг 1	Бензин 1 2		Бензин 2 4	
	мг/ч 3	%	мг/ч 3	%
0,00	25	100	22	100
0,41	30	120	25	114
0,82	39	156	35	159
1,64	67	267	65	295

KEY: 1 -- Concentration of TEL in gasoline, g/kg
2 -- Gasoline 1
3 -- mg/hr
4 -- Gasoline 2

deposits leads to misfirings in spark plug operation due to electrode short-circuiting. An effective means of controlling this phenomenon is the addition of phosphorus additives. A compound of phosphorus with lead -- -- $Pb_3(PO_4)_2$ -- remains nonelectroconductive up to extremely high temperatures (Fig. 66). The use of a phosphorus additive (tricresylphosphate) when an engine is run on ethyl gasoline permits an extension of the operating time of spark plugs with no electrode short-circuiting by more than a factor of 2 (Fig. 67).

It must also be noted that lead deposits exhibit increased hygroscopicity. As a result, due to the accumulation of moisture after prolonged standing of a motor vehicle, misfirings are possible in spark plug operation when an engine is being started up.

4. When ethyl automotive gasolines are used, lead deposits may possibly form on the support surfaces of valves and seats. These deposits disrupt the normal seating of valves, which leads to an inrush of hot gases into the engine exhaust system. At the inrush sites, the valve temperature rises sharply, and the bevel face of the part may be scorched. The just-begun "scorching" of a valve will continue until this part totally malfunctions.

The above-noted phenomena are controlled mainly by selecting the appropriate heat-resistant alloys and improving the design of the exhaust system. All measures are taken to cool the exhaust valve as best as possible.(sodium cooling, and so on). Good results are provided by the "self-cleaning" of the bevel of the valve as it is rotated.

5. When ethyl gasoline evaporates in the carburetor of an engine, the amount of TEL entering each cylinder proved to be dissimilar. In addition to the nonuniform distribution of TEL, the nonuniform distribution of the scavenger as well is observed. Thus, the most common scavenger --ethyl bromide (R-9 fluid) -- boils at 34.4° C. It vaporizes together

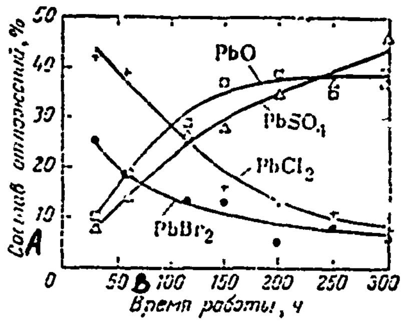


Fig. 64. Variation in chemical composition of deposits with time /111/

KEY: A -- Composition of deposits, %
B -- Operating time, hours

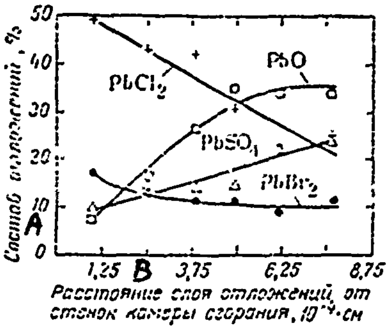


Fig. 65. Composition of deposits at various distances from combustion chamber walls /111/

KEY: A -- Composition of deposits, %
B -- Distance of deposit layer from combustion chamber walls, 10^{-4} cm

with low-boiling fractions, while TEL remains with the high-boiling fractions in the liquid film. The above-noted nonuniformity in the distribution of various fractions leads to a mixture with excess TEL and a deficiency in the scavenger entering some cylinders, while the opposite is the case in others. In the cylinders where there is not enough scavenger, deterioration of the removal of TEL combustion products is observed along with an increase in deposit formation. Excess scavenger leads to an increase in the corrosion of engine parts.

The most uniform distribution can be achieved by using a scavenger whose boiling point is close to the boiling point of the antiknock. From these considerations, acetylene tetrabromide has been proposed as a scavenger for gasolines containing TEL; it has a volatility close to that of TEL. Engine tests showed very good results, but acetylene tetrabromide proved to be unstable in storage, and unfortunately it had to be rejected. Good distribution by cylinders is provided by dibromopropane that is part of P-2 ethyl fluid.

Dibromoethane also has a fairly high boiling point (132° C and is distributed by engine cylinders better than ethyl bromide. However, dibromoethane has another disadvantage -- a high melting point (10° C). At air temperatures below 0° C, dibromoethane crystallizes from solution, and the ethyl fluid becomes heterogeneous and unsuitable for use.

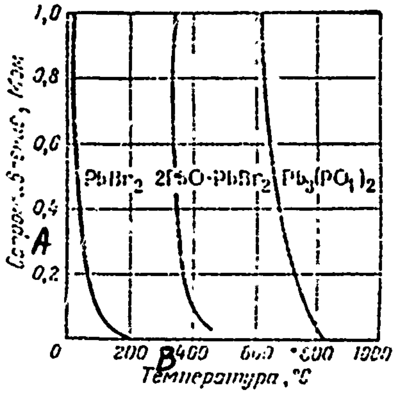


Fig. 66. Dependence of electrical resistance of various lead compounds contained in deposits on temperature /109/

KEY: A -- Resistance, megaohms
B -- Temperature, °C

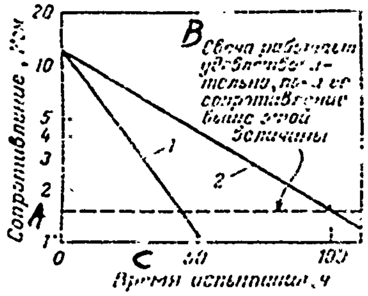


Fig. 67. Dependence of the electrical resistance of spark plug on test duration /110/:

1 -- ethyl gasoline not containing additive
2 -- ethyl gasoline containing tricresylphosphate

KEY: A -- Resistance, megaohms
B -- Spark plug functions satisfactorily until its resistance is higher than this value
C -- Test time, hours

The high volatility of ethyl bromide, in addition to nonuniform distribution, is the reason for the vaporization of some of the scavenger when gasoline is in storage. When gasoline is stored in the summer, especially in the southern regions, much of the ethyl bromide can evaporate. When this kind of gasoline is used in an engine, there is not enough scavenger to combine with and remove all the TEL combustion products formed, and the amount of lead deposits can rise steeply.

6. One of the typical features of ethyl gasolines is their ability to corrode metals when water is present. Halogeno-organic compounds used as scavengers react with water, forming hydrohalogenide acids. These acids corrode galvanized iron, magnesium alloys, and to a lesser extent -- aluminum and bronze. The greatest metal corrosion is usually observed at the interface of the gasoline layer with the water layer. Metal in contact only with water or only with gasoline corrodes to a lesser extent. Water, by removing some of the scavenger, disturbs the ratio between the TEL and

the scavenger, which leads to an increase in deposit formation when these kinds of gasolines are used. The storage of ethyl gasolines on water blankets is categorically forbidden. Hydrohalogenide acids can form as the result of scavenger decomposing at elevated temperatures in combustion chambers. In particular, hydrogen bromide even when in the vapor state exhibits high activity and is capable of corroding metals. Traces of this "hot" corrosion can usually be observed at the seats, spark plugs, and guide liners of exhaust valves.

However, the greatest corrosive action of hydrohalogenide acids formed during combustion is observed upon prolonged engine stoppages when the acids are able to dissolve in water condensed from combustion products. After a time, traces of corrosion can be detected at the locations of water settling in the form of shallow pittings in the metal. Therefore when it is necessary to place an engine for preservation after having been run on ethyl gasoline, special preservative lubricants must be used.

7. At ordinary temperatures of storage and use, tetraethyl lead undergoes oxidation by air oxygen, forming gasoline-insoluble products. Ethyl gasoline can become cloudy when stored. Fine suspended particles appear in it, settling out with time at the bottom of the container in the form of easily disturbed white precipitate. Examination of the precipitate showed that it consists mainly of compounds of lead formed in the oxidation and decomposition of TEL.

The mechanism of TEL oxidation in gasoline can be represented thusly [113]. The first stages of decomposition of TEL were the formation of free radicals:

$$Pb(C_2H_5)_4 \longrightarrow \dot{P}b(C_2H_5)_3 + \dot{C}_2H_5$$

Ethyl radicals can participate in volumetric reactions with hydrocarbon molecules or react themselves with oxygen, forming peroxide radicals:

$$\dot{C}_2H_5 + O_2 \longrightarrow C_2H_5-O-\dot{O}$$
$$\dot{R} + O_2 \longrightarrow R-O-\dot{O}$$

Peroxide radicals form hydroperoxides and new radicals:

$$R-O-\dot{O} + R_1-H \longrightarrow R-O-O-H + \dot{R}_1$$

The tetraethyl lead radical can react with the hydroperoxide:

$$R-O-O-H + (C_2H_5)_3\dot{P}b \longrightarrow (C_2H_5)_3PbOH + R-\dot{O}$$

or

$$R-O-O-H + (C_2H_5)_3\dot{P}b \longrightarrow (C_2H_5)_3PbOR + \dot{O}H$$

Triethyl lead compounds can dissociate, forming free radicals of diethyl lead:

$$(C_2H_5)_3PbOH \rightarrow (C_2H_5)_2\dot{P}bOH + \dot{C}_2H_5$$

The diethyl lead radical can react with hydroperoxide, forming compounds of diethyl lead that are wholly soluble in gasoline:

$$(C_2H_5)_2\dot{P}bOH + R-O-O-H \rightarrow (C_2H_5)_2Pb(OH)(OR) + \dot{O}H$$

This scheme accounts for the dissimilar stability of TEL in solutions of hydrocarbons of various structures. TEL is most stable in alkylate and catalytic cracking gasolines, and least stable -- in alkylbenzene. In isooctane, the stability of TEL is much higher than in the remaining hydrocarbons. TEL is oxidized and decomposed relatively slowly in unsaturated hydrocarbons and in mixtures with other hydrocarbons.

The varying behavior of TEL is evidently associated with the stability of the peroxide compounds of hydrocarbons of various structural classes and with their ability to react with TEL.

This scheme also accounts for the effect of temperature and of TEL concentration in gasolines on their stability. As temperature is increased, the extent of TEL dissociation rises, and therefore so does the number of free radicals initiating the oxidative process. The number of free radicals increases also with increase in TEL concentration in gasoline.

Decomposition of TEL is particularly accelerated by the action of sunlight. Usually, when gasoline is in storage or in use, it is quite reliably protected against sunlight. Nonetheless, sometimes it can be exposed to the more or less prolonged action of sunlight, for example in the open glass cylinder of a gasoline service station pump. In these cases, even after several hours a precipitate of lead deposits can appear. Decomposition of TEL reduces the knock resistance of gasolines. Additionally, the deposit of lead compounds formed hinders the normal use of ethyl gasolines because it clogs filters, gasoline lines, jet nozzles, and so on.

The incipient decomposition of TEL in gasolines progressively accelerates. Ethyl automotive gasolines in which TEL decomposition has just begun can be used as fuel for engines only after careful filtration. After being filtered, the gasoline must be used at once, since TEL decomposition will continue [114].

The most effective means of protecting against TEL decomposition in ethyl gasolines is to add special additives: anti-oxidants [113-116] and metal deactivators [117, 118]. Only agents which yield inactive compounds not only with hydrocarbon, but also with alkyl lead radicals supplied by TEL can be used as anti-oxidants for ethyl gasolines.

The anti-oxidants proved to be an effective way of preventing the decomposition of TEL not only when ethyl gasolines are in storage, but also when ethyl fluids are stored [115]. Accordingly, the anti-oxidant p-hydroxydiphenylamine was incorporated in the composition of domestic ethyl fluids. Abroad, TEL is stabilized by anti-oxidants such as 2,6-di-ter-butyl-4-methylphenol, 2,4-dimethyl-ter-butylphenol, N, N'-di-sec-butyl-p-phenylenediamine, and so on.

In the practice of ethyl gasoline storage and use, one must remember that anti-oxidants only retard the oxidation and decomposition of TEL, and the possibility of these processes occurring is not obviated.

8. The most substantial disadvantage of ethyl gasolines is their toxicity. Ethyl fluid, as well as pure tetraethyl lead, is a persistent strong-acting poison. Working with ethyl fluid and especially adding it to gasolines (ethylation) must be carried out with careful compliance of all precautionary regulations. Therefore gasolines are ethylated only at the refineries where there is special mixing equipment. Ethylation or final ethylation of gasolines without special equipment threatens poisoning and is therefore categorically forbidden.

The TEL content in ethyl gasolines is very low and the toxicity is many times less than the toxicity of ethyl fluid. Many years of experience in the use of ethyl automotive gasolines the world around showed that when elementary rules of precaution are observed, the harmful effect of TEL on the human organism can be completely avoided.

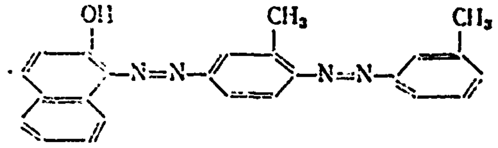
To prevent use for undesignated functions, ethyl gasolines are dyed. For convenience in use, various grades are colored differently. In accordance with GOST 2084-67, domestic automotive gasolines must have the following colors: A-66 -- orange, A-76 -- green, AI-93 -- blue, and AI-98 -- yellow.

Domestic R-9 ethyl fluid is colored yellow. To do this, a dye is added -- 0.422 g per kg of ethyl fluid.

For a long time dyes such as fat-soluble yellow 2Zh (dimethylaminoazobenzene) and fat-soluble dark-red Sudan IV (the product of the combination of beta-naphthol with o-aminoazotoluene) were long used in coloring gasolines. Domestic and foreign research established that these dyes have increased carcinogenic activity. Accordingly, new dyes free of carcinogenic properties were developed and tested [119].

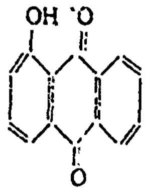
Diethylaminoazobenzene, called fat-soluble yellow K, has been proposed instead of fat-soluble yellow 2Zh:

The product of the reaction of beta-naphthol and m-aminoazotoluene, called fat-soluble dark-red Zh has been proposed instead of fat-soluble dark-red Sudan IV:

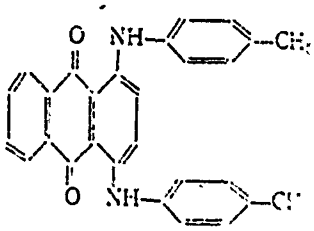


The new dyes underwent comprehensive tests and are currently being produced and used in dying ethyl fluid and ethyl gasolines.

A mixed dye consisting of 1,8-dioxyanthraquinone and fat-soluble green anthraquinone taken in a ratio of 2:1 was developed to color A-76 gasoline green (MRTU [Interrepublic Specifications] 6-14-68).



9,10-dioxyanthraquinone



green anthraquinone

The mixed dye is added to gasoline in the amount of 10 mg per kg (0.001 percent) in a solution of aromatic hydrocarbons.

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[To Chapter Four]

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CHAPTER FIVE
FRACTIONAL COMPOSITION OF GASOLINES AND ENGINE PERFORMANCE

Fractional composition is one of the most important indicators of automotive gasoline quality. On it depends such engine characteristics as an easy and reliable start, warm-up time, vehicle response, and other operating indicators.

The fractional composition of gasolines is determined by distillation in standardized conditions in a special instrument. 100 ml of a gasoline is heated in the flask of the instrument with a gas burner and on a thermometer the temperatures at which certain amounts of gasoline begin to distill are recorded. The distillation temperatures for 10, 50, and 90 percent of gasoline and its end boiling point are recorded for automotive gasolines. For research purposes, it is customary to record the distillation temperature of each 10 percent of the gasoline. Then, based on these data a gasoline distillation curve is plotted in the following coordinates: amount of gasoline versus temperature.

All the requirements of modern carburetor engines on the fractional composition of fuels used can be divided into requirements associated with climatic conditions of vehicle use and requirements dictated by engine design characteristics.

The ability of a gasoline to ensure rapid acceleration of a vehicle, minimum fuel expenditure, uniform qualitative and quantitative distribution of the mixture by engine cylinders, and minimum wear of the piston-cylinder group represents a far-from-complete list of the requirements on fractional composition associated chiefly with engine design characteristics. The matching of these requirements and the quality of the gasolines used is achieved both by improving the physicochemical indicators of gasolines and by improving the design of carburetors, intake systems, and combustion chambers.

Clamatic conditions of vehicle use in different parts of our country in different times of the year impose two main requirements on the fractional composition of gasolines -- the reliable starting of an engine at the lowest possible air temperatures and prevention of trouble in engine feed systems associated with partial evaporation of gasoline at high air temperatures. Here must also be included the problem of combating icing of carburetor parts by varying gasoline fractional composition.

Many of the above-listed requirements imposed on the fractional composition of gasolines are by their nature mutually contradictory and can be satisfied only by a compromise solution.

Starting a Cold Engine

General principles. The difficulties in starting a cold carburetor engine during winter at low ambient air temperatures are due to three main reasons: worsening of the gasoline volatility, a rise in viscosity of the lubricating oil, and a drop in the capacitance and voltage of the storage batteries. In addition to these main reasons, starting a cold engine is hindered owing to increased leakage of the combustible mixture through the gaps, more intense heat transfer to the combustion chamber walls, low intake air temperature, and thus, low mixture heating temperature after compression, and so on.

Until recently the main problem in starting a cold engine was to select the appropriate oil. At the present time so-called thickened oils have been developed and thoroughly tested; their use ensures engine crankshaft rotation at the required starting rpm at low temperatures. During the testing of thickened oils in a cold chamber, it was often noted that in spite of the fairly high starting rpm, an engine cannot be started owing to the poor volatility of the gasoline.

A problem of starting a carburetor engine can be regarded as a set of three independent matters:

-- starting a cold engine without any special accessories by means of the good volatility of the gasolines used;

-- starting a cold engine by using special starting fluids; and

-- starting an engine after preliminary warming with heaters.

In this section we consider only the starting of a cold engine without special accessories. In starting an engine, gasoline volatility in the intake system deteriorates due to the low gasoline temperature and its poor atomization at low air temperatures in the venturi. At the present time, a number of design measures improving engine starting abilities have been developed [1-4]. Starting adjustments of carburetors, improvement in the design of combustion chambers and intake manifolds, and several other methods unquestionably promote better vaporization of gasoline, but the decisive factor is the content of low-boiling hydrocarbons in gasoline. It is precisely these hydrocarbons, on evaporating in the intake manifold, that form the air-fuel mixture capable of spark ignition.

It would appear that the amount of low-boiling fractions must not be limited in fuel intended to start a cold engine. However, an excessive content of these fractions in gasoline causes misfires when a warm engine is started and higher gasoline losses in storage and use. The content of low-boiling fractions in modern automotive gasolines is regulated by the saturated vapor pressure and the 10 percent gasoline distillation temperature.

The literature contains contradictory data on how to introduce into fuel low-boiling fractions required to ensure that a cold engine can be started. N. V. Brusyantsev [5] maintains that to start carburetor engines in winter conditions in the central zone of the USSR when the air temperature is down to -20° C requires that the 10 percent gasoline distillation temperature be not higher than 76-78° C. D. M. Aronov [6], in suggestions on new specifications for domestic automotive gasolines, provides for a reduction in the 10 percent distillation temperature down to 60° C for summer grades of gasolines, and down to 50° C for winter grades. Based on the data of A. S. Irisov [7], A-72 gasoline with a 10 percent distillation temperature below 70° C must ensure cold engine starting down to -17° C, while winter A-66 gasoline with a 10 percent distillation temperature of up to 65° C must ensure cold engine starting down to -24° C.

In Great Britain with the air temperature in winter rarely goes below -7° C, it is believed that to ensure satisfactory cold engine starting it is necessary that 10 percent of the volume be distilled off by 60° C for the winter gasoline grade, and by 70° C -- for the summer grade [8].

In the United States, the ease and reliability of cold engine starting sometimes are associated with the amount of light fractions in gasoline boiling to 70° C [9-11]. It is held that engine starting at an air temperature of -20° C can be achieved without difficulty if gasoline used contains more than 20 percent low-boiling fractions boiling to 70° C.

Starting qualities of various gasolines. To revise requirements on the fractional composition and to study the starting qualities, tests were made of seven gasoline samples with different light-fraction content (Table 55) for the laboratory-vehicle GAZ-51 [12].

In the tests, low-viscous motor oil was used permitting the crankshaft rpm required for engine starting. The engine starting time was recorded with an oscillograph at the first spark, after which the engine began to operate stably.

Table 55. Fractional composition and starting properties of automotive gasoline samples

Показатель 1	Образцы бензинов 2						
Фракционный состав, °C: 3							
$t_{н.к.}$ 4	34	41	43	46	55	56	63
t_{10}	48	59	64	68	75	77	86
t_{20}	55	68	73	78	81	85	92
t_{30}	63	76	80	85	92	93	99
t_{40}	71	88	89	93	100	100	107
t_{50}	81	95	101	103	110	105	113
t_{60}	94	109	113	113	120	118	124
t_{70}	109	126	127	127	131	131	138
t_{80}	129	143	143	143	147	145	151
t_{90}	157	168	168	166	166	165	167
$t_{к.к}$ 5	187	187	187	187	187	187	189
Давление насыщенных паров 6 (ГОСТ 1756—52), *мм рт. ст.*	547	430	310	250	203	191	189
Предельная температура воздуха, при которой возможен пуск холодного двигателя $t_{в}$, °C ниже нуля 7	26–27	21–22	18–19	16–17	12–13	11–12	7–8

Key:
1 -- Indicator
2 -- Gasoline samples
3 -- Fractional composition
4 -- $t_{i.b}$
5 -- $t_{e.b}$
6 -- Saturated vapor pressure (GOST 1756-52), mm Hg
7 -- Maximum air temperature at which a cold engine can be started up, t_a, ° C below zero

Fig. 68 shows the dependence of the air temperature at which engine starting is possible on the gasoline fractional composition.

The limiting engine starting temperatures for gasolines of various fractional compositions proved to be virtually directly proportional to the initial boiling temperature and the 10 percent gasoline distillation temperature (Fig. 68).

The possible engine starting temperatures found are much lower than those indicated by Braun [13] and are somewhat lower than those determined by Cowberay and Witters [14] and by Unselman and Forster [15] (Table 56).

Based on these results, for practical purposes one can recommend the following empirical formula for determining the air temperature at which engine starting is possible, as a function of the 10 percent gasoline distillation temperature:

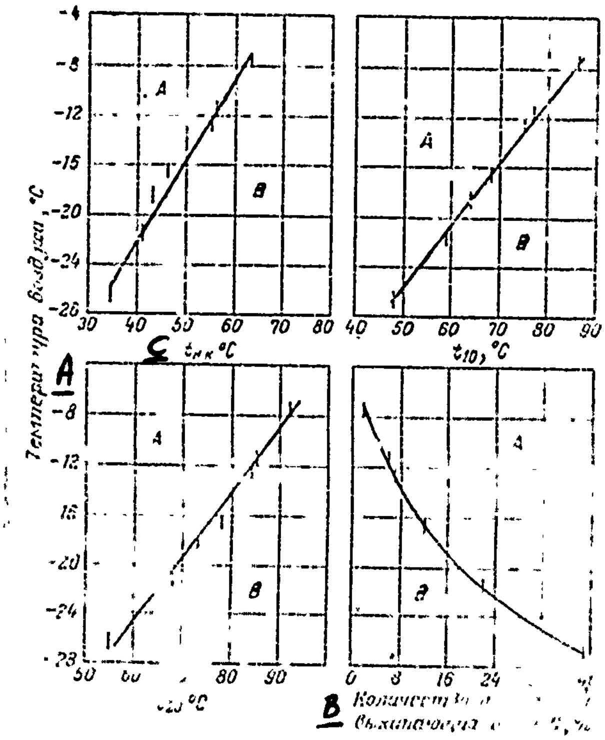

Fig. 68. Dependence of air temperature at which engine starting is possible on the fractional composition of gasolines
A and B -- corresponding to regions in which a cold engine can and cannot be started up
Key: **A** -- Air temperature
B -- Amount of light fractions boiling to 72° C
C -- $t_{i.b}$

$$t_a = \frac{1}{2} t_{10} - 50{,}5$$

Some investigators believe that the starting qualities of automotive engines are characterized not only by the content of the lowest-boiling fractions (10 percent of the gasoline), but also by the amount of the higher-boiling fractions and, in particular, by the 20 percent gasoline distillation temperature [16].

The dependence of the starting qualities of the gasolines tested (cf. Table 55) on the 20 percent distillation temperature also is virtually linear (Fig. 68) and is closely described by the following formula:

Table 56. Comparison of the results of various studies on the effect of the 10 percent gasoline distillation temperature on gasoline starting properties

t_{10}, °C	1 $t_{в}$, °C			
	[illegible]	[11]	[13]	[illegible]
48	—22	—26	—27	2 [illegible]—2 минус 27
59	—12	—19	—19	2 минус 22—2 минус 23
64	—8	—15	—16	2 минус 18—2 минус 19
68	—5	—13	—13	2 минус 16—2 минус 17
75	—1	—8	—9	2 минус 12—2 минус 13
77	+3	—7	—8	2 минус 11—2 минус 12
86	+10	—1	—6	2 минус 7—2 минус 8

Key: 1 -- t_a

2 -- Minus

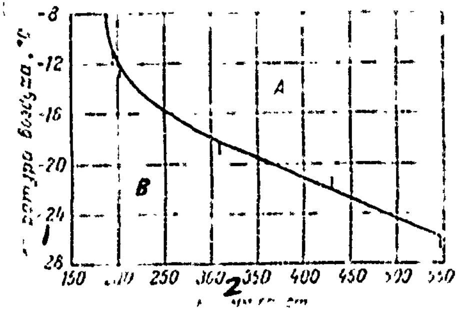

Fig. 69. Dependence of air temperature at which engine starting is possible on the gasoline saturated vapor pressure

A and B -- correspond to regions in which engine starting is and is not possible

Key: 1 -- Air temperature

2 -- p_{sat}, mm Hg

$$t_a = \frac{1}{2} t_{20} - 55{,}0 \quad .$$

We have already stated that American workers associate the starting qualities of gasolines with their content of light fractions boiling to 70° C. This new approach to rating the starting qualities of gasolines, based as it is not on determining the distillation temperature of some amount of gasoline, but on determining the amount of gasoline boiling up to a certain temperature, undoubtedly deserves attention.

The data obtained on the maximum engine starting temperatures as a function of the amount of light fractions boiling to 70° C are presented in Fig. 68. This function is not linear. As the ambient air temperature is decreased, the requirement for fractions boiling to 70° C rises more rapidly. Evidently, it is useful in the future when accumulating data for the standard distillation of commercial automotive gasolines, to note the amount of light fractions boiling to 70° C, and to introduce into the specifications for gasoline the following index: the amount of gasoline in percent distilling to 70° C.

The tests conducted show the highly characteristic dependence of the temperature of possible engine starting on the saturated vapor pressure of the gasolines tested (Fig. 69). When the saturated vapor pressure of gasoline is reduced to 250 mm Hg, its starting qualities deteriorate. A reduction in the saturated vapor pressure below 250 mm Hg is accompanied by a severe deterioration in starting qualities. These results indicate the necessity of limiting not only the upper, but also the lower limits of the saturated vapor pressure of gasolines. Commercial automotive gasolines of all kinds have a saturated vapor pressure not below 250 mm Hg.

All the above-presented results are plotted for gasolines whose low-boiling fractions contain practically no butanes. In recent years, in the course of various tests made on automotive gasolines it was noted that when butanes are added, the starting qualities of gasolines improve not proportional to the change in the specific indicators of their volatility. In other words, the starting qualities of a gasoline containing butane always proved to be better than the starting qualities of a gasoline not containing butane, but with the same saturated vapor pressure and with the same 10 percent distillation temperature. The above-proposed formulas for the case of gasolines containing butanes give overstated values for the air temperature at which cold engine starting is possible.

Improvement in the starting qualities of gasolines by adding butanes indicates the vital importance not only of the amount but also of the kind of low-boiling components contained in commercial gasolines.

Effect of low-boiling components. Modern automotive gasolines are prepared by blending various components, whose quality and quantity depend both on the grade of gasoline and on the total balance of petroleum products produced at the refinery.

Base components of automotive gasolines as a rule contain small amounts of low-boiling fractions; therefore, low-boiling components are specially added to commercial gasolines. Components used at various refineries sometimes differ widely in their properties, but they nonetheless can still be classified provisionally into three groups.

The first group must include the lowest-boiling components, which are gases at ordinary temperatures. The so-called spent butane-butylene fraction obtained after alkylation in this group is widely used. This fraction includes about 90 percent normal butane, a small amount (2-4 percent) isobutane, and 5-8 percent pentanes. The saturated vapor pressure of this fraction depends on its composition and varies within fairly wide limits (2000-2800 mm Hg).

The second group can include narrow fractions containing predominantly some low-boiling individual hydrocarbon which remains liquid in ordinary conditions. Technical isopentane (2-methylbutane) has found application, from among the components in this group. Unitl recently isobutane was used as an aviation gasoline component, but in recent years it has found growing use in the compounding of automotive gasolines, especially of the higher grades.

And, finally, the third group of components must be regarded as including fairly broad fractions of low-boiling hydrocarbons. Various natural gasolines, pentane-amylene fractions, and so on from this group are widely used. The composition and properties of the group components are extremely inconstant and vary within quite wide limits in the gasolines from different refineries.

The possibilities for increasing the saturated vapor pressure and lightening the fractional composition gasolines by adding the most characteristic of the above-listed three groups of automotive gasoline components were tested for the butane fraction (containing about 90 percent C_4, and saturated pressure 2600 mm Hg), technical isopentane (initial boiling 27° C, 10 percent boiling 28° C, 50 percent boiling 29° C, 90 percent boiling 34° C, and end boiling 34° C, and saturated vapor pressure 1010 mm Hg), and natural gasoline (initial boiling 23° C, 10 percent -- 28° C, 50 percent -- 40° C, 90 percent -- 77° C, and end boiling -- 80° C,wwith the saturated vapor pressure at 1140 mm Hg).

The above-listed components were added in different amounts to two gasoline samples. Thermal cracking gasoline had an initial saturated vapor pressure of 360 mm Hg (0.2 percent content of C_4 hydrocarbons). The saturated vapor pressure is representative of many base automotive gasolines and the addition of light components to the selected thermal cracking gasoline sample made it possible to evaluate the potential of these components in compounding commercial gasolines. The second gasoline sample (platforming gasoline) had a fairly high initial saturated vapor pressure (about 560 mm Hg), and

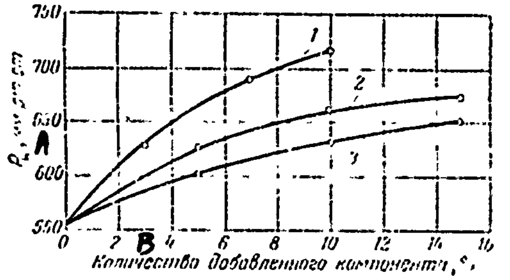

Fig. 70. Variation in the saturated vapor pressure of platforming gasoline with the addition of the following components:

1 -- butane
2 -- natural gasoline
3 -- isopentane
Key: A -- P_{sat}, mm Hg
B -- Amount of component added

when low-boiling components were added to it, they were shown to be capable of producing special lightened, northern samples of automotive gasolines with improved starting qualities (the initial platforming gasoline depended about 3 percent C_4 hydrocarbons).

Fig. 70 presents the saturated vapor pressure of gasolines as functions of the amount of low-boiling components added. The greatest rise in saturated vapor pressure, as to be expected, was observed when butane was added, and the smallest -- when isopentane was added; natural gasoline is intermediate. Adding 7 percent butane to thermal cracking gasoline also gives the same rise in the saturated vapor pressure as the addition of 10 percent natural gasoline or 13 percent isopentane.

All low-boiling components cause a greater rise in the saturated vapor pressure when added to a gasoline that had a lower initial saturated vapor pressure. Thus, adding 1 percent n-butane raised the saturated vapor pressure of thermal cracking gasoline (P_{sat} = 360 mm Hg) by an average of 40 mm Hg, while the addition of this amount of component to platforming gasoline (P_{sat} = 560 mm Hg) raise the saturated vapor pressure by an average of 20 mm Hg (cf. Fig. 70).

It must be noted that the literature contains contrasting data on the effectiveness of butane in raising the saturated vapor pressure of gasolines. Thus, from the data of M. B. Wolf et al., each percentage of butane added raises the saturated vapor pressure by 25-30 mm Hg; work done by Unselman and Forster [15] showed that adding 1 percent butane causes a 35-45 mm Hg

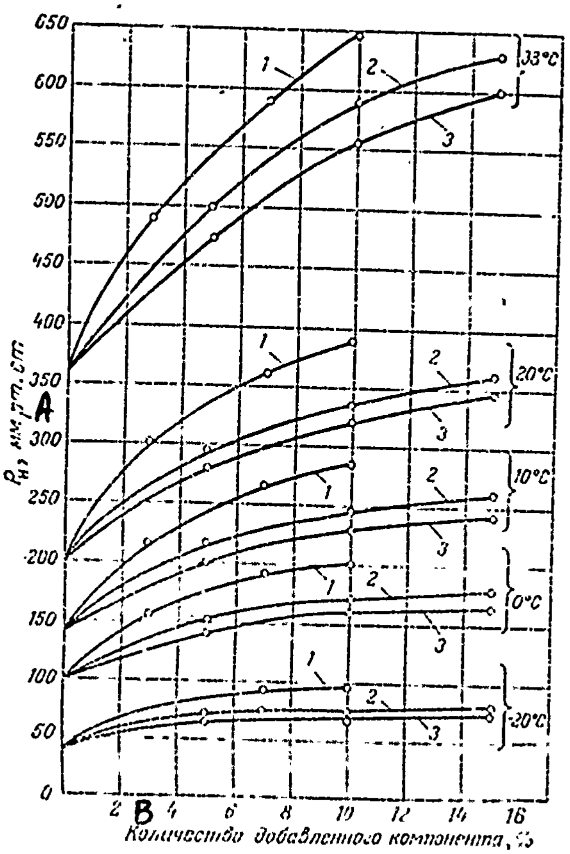

Fig. 71. Temperature dependence of saturated vapor pressure of thermal cracking gasoline when various components are added:

1 -- butane
2 -- natural gasoline
3 -- isopentane

Key: A -- P_{sat}, mm Hg

B -- Amount of component added

rise in the saturated vapor pressure. Obviously, the difference in the data published in the literature is a consequence of using gasolines with different initial saturated vapor pressures. Fig. 70 shows that as the saturated vapor pressure of the gasoline is increased, each new unit of pressure rise requires adding an increasing amount of low-boiling components. This factor must be reckoned with in preparing special northern grades of automotive gasolines.

To evaluate the starting qualities of automotive gasolines and to find the rule of various hydrocarbons in improving these properties, one must trace the change in the saturated vapor pressure with temperature in the presence of various low-boiling components. The results for thermal cracking gasoline are presented in Fig. 71.

With decrease in temperature, besides the reduction in the saturated vapor pressure, there is a smaller absolute difference for this indicator as between various gasolines; the effectiveness of components in increasing the absolute saturated vapor pressure of gasoline becomes less.

It must be noted that with decrease in temperature, the relative effectiveness of butane rises markedly. Thus, when 7 percent butane is added to thermal cracking gasoline, the saturated vapor pressure at -20° C increases by about twofold. The effectiveness of natural gasoline and isopentane at -20° C is much less. These results then account for the high effectiveness of butane in improving the starting qualities of gasolines.

Using the Clausius-Clapeyron equation, we can represent the saturated vapor pressure as a linear function of temperature in semilogarithmic coordinates [17]:

$$\lg P_{sat} = -\frac{A}{T} + B$$

where A and B are constants.

Knowing saturated vapor pressures at the two temperatures, we can find the slope of the line:

$$\lg P'_{sat} = -\frac{A}{T_1} + B$$

$$\lg P^{2}_{sat} = -\frac{A}{T_2} + B$$

$$\lg P'_{sat} - \lg P^{2}_{sat} = -\frac{A}{T_1} + \frac{A}{T_2}$$

$$\lg P'_{sat} = \lg P^{2}_{sat} - A\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The coefficient A characterizes the slope of the line, $\lg P = f\left(\frac{1}{T}\right)$ to the 1/T axis.

A. S. Irisov [17] shows the applicability of the Clausius-Clapeyron equation for gasolines not containing low-boiling components and with low saturated vapor pressures. The saturated vapor pressure was determined by him for a vapor/liquid phase ratio of 4:1. The results (Fig. 72) show that

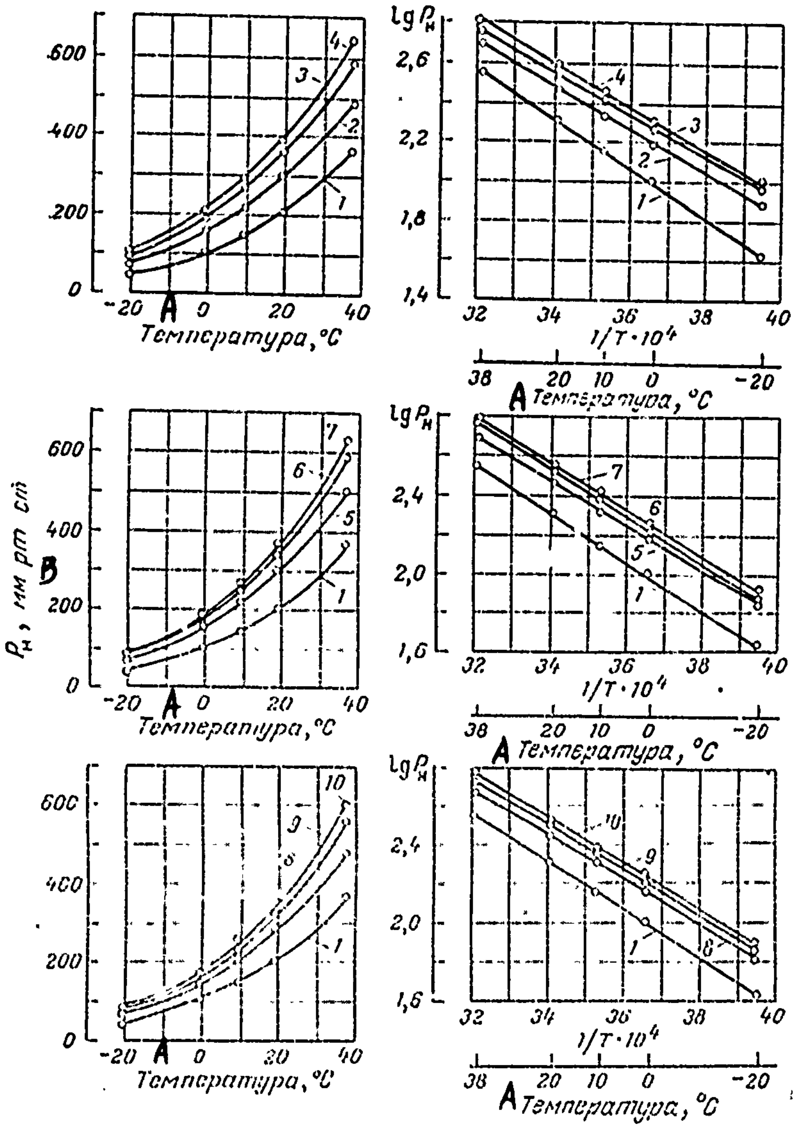

Fig. 72. Dependence of saturated vapor pressure of thermal cracking gasoline on temperature:

1 -- initial gasoline
2 -- as above + 3 percent butane
3 -- as above + 7 percent butane
4 -- as above + 10 percent butane
5 -- as above + 5 percent natural gasoline
6 -- as above + 10 percent natural gasoline
7 -- as above + 15 percent natural gasoline
8 -- as above + 5 percent isopentane

[continued on following page]

[Continuation to Fig. 72 on preceding page]

9 -- as above + 10 percent isopentane
10 -- as above + 15 percent isopentane
Key: A -- Temperature
B -- P_{sat}, mm Hg

Table 57. Effect of light components on the fractional composition and saturated vapor pressure of gasoline

Образец 1	$t_{н.к.}$, °C 2	t_{10}, °C	t_{50}, °C	t_{90}, °C	$t_{к.к.}$, °C 3	До 70° С выкипает, % 4	$P_{н}$, мм рт. ст. 5
Бензин термического крекинга 6	48	67	112	162	182	12,0	360
с 3% бутана 7	37	60	111	161	180	16,5	490
с 7% бутана 8	31	55	110	162	181	20,0	590
с 10% бутана 9	29	52	109	163	181	22,5	645
с 5% газового бензина 10	41	58	103	161	179	21,0	500
с 10% газового бензина 11	35	53	101	161	180	26,5	590
с 15% газового бензина 12	31	48	94	161	178	32,5	630
с 5% изопентана 13	43	58	107	161	179	20,0	475
с 10% изопентана 14	37	53	98	161	178	27,0	555
с 15% изопентана 15	34	47	94	160	176	32,0	600
Бензин платформинга 16	38	55	90	141	166	29,0	560
с 3% бутана 7	33	50	85	141	165	33,0	530
с 7% бутана 8	30	46	81	145	165	35,0	690
с 10% бутана 9	25	43	83	143	161	38,0	715
с 5% газового бензина 10	34	50	86	141	164	33,0	625
с 10% газового бензина 11	31	45	82	142	161	38,5	660
с 15% газового бензина 12	29	43	80	142	164	41,5	575
с 5% изопентана 13	26	50	87	143	165	32,0	600
с 10% изопентана 14	33	46	85	142	164	37,0	630
с 15% изопентана 15	31	44	80	140	163	40,0	650

Key: 1 -- Sample
2 -- $t_{i.b}$
3 -- $t_{e.b}$
4 -- Boiling up to 70° C
5 -- P_{sat}, mm Hg
6 -- Thermal cracking gasoline
7 -- with 3 percent butane
8 -- with 7 percent butane
9 -- with 10 percent butane
10 -- with 5 percent natural gasoline
11 -- with 10 percent natural gasoline
12 -- with 15 percent natural gasoline
13 -- with 5 percent isobutane
14 -- with 10 percent isobutane
15 -- with 15 percent isobutane
16 -- Platforming gasoline

even for gasolines with high initial saturated vapor pressure, the dependence of lg P_{sat} on $1/T$ is linear. Adding low-boiling components somewhat changes the slope of the line, but does not affect the linearity of the function.

The slope of the lines lg P_{sat} as a function of $(1/T) \cdot 10^4$ lies within the range 1090-1270. The linear dependence of lg P_{sat} on $1/T$ persists also for saturated vapor pressure determined for a 1:1 phase ratio,

Data on the effect of adding butane, natural gasoline, and pentane on the effect of composition of gasolines are shown in Table 57.

From the table it is clear that adding butane sharply lowers the initial boiling part of gasoline. The remaining points of the fractional composition (10 percent gasoline distillation temperature and the amount of gasoline distilling to 70° C) vary roughly the same for the addition of each low-boiling component. Thus, the presence of butane in gasoline is reflected first of all in the initial boiling point of the gasoline. It is precisely this indicator that characterizes the presence of butane, and, to some extent, its amount. This factor points to the necessity of resorting to determining and standardizing the initial boiling point of gasolines.

With reference to the results, and also with reference to the data on the starting tests made of gasolines containing butanes, the earlier-derived formula for the dependence of the air temperature at which cold engine starting is possible on the distillation temperature of 10 percent of gasoline not containing butanes takes on the following form for butane-containing gasolines:

$$t_a = \frac{1}{2} t_{10} - 50,5 + \frac{(t_{i.b} - 50)}{3}$$

Still, it is obvious that for practical purposes when the composition and origin of gasolines are unknown, one must use the formula derived for gasolines not containing butanes. The air temperature calculated by this formula will be the temperature at which cold engine starting is indeed possible for gasoline having any composition. In the case when butanes are present in a gasoline, the true starting temperature will be somewhat lower.

In all the above-presented material for rating the starting qualities of automotive gasolines, we used the temperature limit of engine starting. This indicator is most convenient, since it directly lets us estimate the starting qualities of gasolines. However, this indicator is not precise enough, since it depends not only on the quality of the gasoline, but also on the design features of the given engine, oil grade, state of the storage batteries, and so on.

At the present time, attempts have been made to relate the starting qualities of a gasoline with its physical properties, and thereby canceling

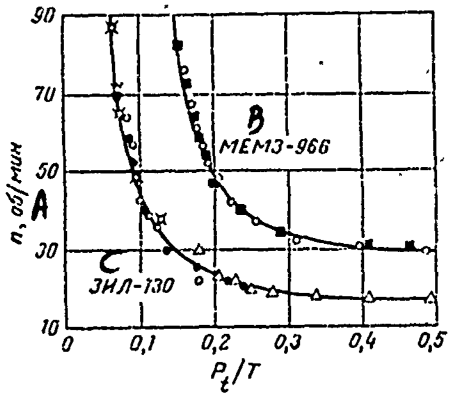

Fig. 73. Dependence of minimum starting engine rpms on the ratio of gasoline saturated vapor pressure at the starting temperature to the starting temperature

Key: A -- rpm
B -- MYeMZ-966
C -- ZIL-130

out the effect of all of the factors. Thus, in rating the starting qualities of fuels, it is customary to subdivide starting into reliable and possible. By reliable starting we mean starting a completely cold engine in not more than three tries, of 10 seconds each, with an interval between the tries of 1 minute with the starter powered by a cold storage battery at 75 percent charge. By possible starting, we mean starting a cold engine under the same conditions, but with the starter powered with a warm, fully charged storage battery. This classification of starting situations allows us to cancel out the effect of the condition of the storage battery.

To clear the starting qualities of gasolines having different fractional compositions, it has been propsed to use an indicator such as the minimum crankshaft rpm in starting. The minimum rpm depends only on the design features of the given engine and on gasoline quality.

A. N. Moiseychik [3] related the minimum starting crankshaft rpm with the ratio of the gasoline saturated vapor pressure, at the starting temperature, to the starting temperature. Experimental data on gasolines with different fractional compositions obtained for two engines are shown in Fig. 71. Noteworthy is the identical trend of the curves obtained for widely differing engines. The ZIL-130 engine, liquid-cooled, eight-cylinder, V-type, with a 6.0 liter capacity, and the MeMZ-966A engines -- air-cooled, four-cylinder, V-type, with a working volume of 0.887 liter. The MeMZ-966A engine exhibits greater unevenness in mixture distribution by cylinders in starting regimes than does the ZIL-130 engine. The extremely similar trend of the curves (cf. Fig. 73) allows us to assume that their position as a function of the engine design characteristics, and that the nature of the curves is determined by gasoline properties. The functions found (cf. Fig. 73) are expressed by A. N. Moiseychik [3] by the following empirical formula

$$n_{min} = A + \frac{1}{\frac{p_t}{2T} - B}$$

where A and B are constants dependent on the design characteristics of the engine and the carburetor; p_t is the saturated vapor pressure of gasoline at the starting temperature, mm Hg; and T is the engine starting temperature, ° K.

The proposed formula relates the starting properties with gasoline saturated vapor pressure. However, its validity for other engines and gasolines having different compositions, just as the interpretation of the physical meaning of this function, requires further investigation.

Vapor Locks

When motor vehicles are operated in the southern regions of our country on especially hot days, quite often cases of spontaneous engine stopping due to vapor locks in the feed system are observed [18, 19]. In a tropical climate, this effect is sometimes massive in scope [20-31]. Vapor lock formation has long been known; the main research in this area was conducted on aircraft where the mean reason for the occurrence of vapor lock is the evaporation of gasoline due to reduced atmospheric pressure. In automotive engines, vapor lock forms due to heating of gasoline in the fuel system, therefore the results of research done in the aviation industry are only partially applicable to motor vehicles.

Tendency of various gasolines to vapor lock formation. Investigations and generalization of literature data afford the following explanation for the appearance of vapor locks and the associated engine malfunctions. When gasoline is heated in a feed system, the lowest-boiling hydrocarbons are evaporated, forming vapor whose volume is 150-200 times greater than the volume of the vaporized gasoline. In these conditions, a mixture of gasoline liquid and vapor forms with the little air that was previously present in the gasoline and which was evolved from it upon heating. The gravimetric capacity of the fuel pump is reduced and the combustible mixture entering the engine becomes leaned. The engine stops. All the troubles seem to be exactly the same as in the case of fuel lock unplugging, and thus the phenomenon began to be called "vapor lock."

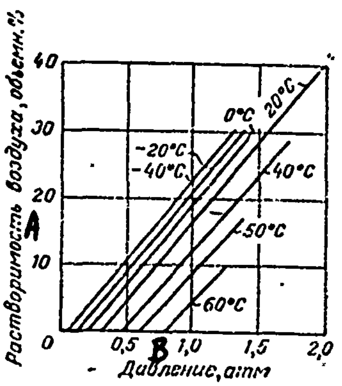

Fig. 74. Solubility of air in gasoline at various pressures and temperatures [29]
Key: A -- Solubility of air, percent by volume
B -- Pressure, atm

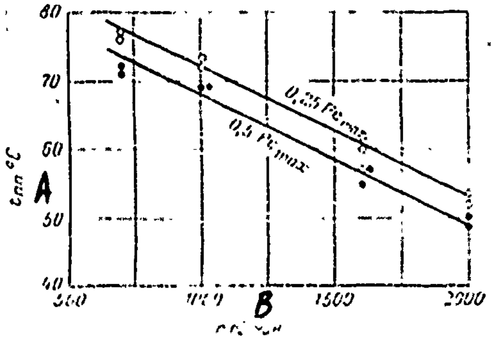

Fig. 75. Dependence of gasoline temperature at which vapor locking develops on rpm and load for a ZIL-120 engine
Key: A -- $t_{v.1}$
B -- rpm

The formation of vapor locks in the feed system depends on the volatility of gasoline, the temperature and pressure of the gasoline in the system, the handling capacity of the fuel system, and gasoline consumption (engine operating regime). A decisive factor determining the formation of vapor locks is the heating temperature of the gasoline. Some workers [18] attribute too great a role in vapor lock formation to the air dissolving in gasoline and evolve from it upon heating. Available data (Fig. 74) shows that when gasoline is heated, the volume of the evolved air can be at most 20-25 percent of the gasoline volume, while the volume of the vapor formed is 150-200 times greater than the volume of the same amount of gasoline remaining in the liquid phase.

The heating temperature of gasoline in an automotive fuel system depends on the design characteristics of the system and the ambient air temperature. The air temperature in the space under the hood is usually somewhat higher than the ambient air temperature. Thus, from tests data with the air temperature at about 40° C, the air temperature under the hood rises to 90-95° C, while the gasoline is heated to 70-75° C. Especially high gasoline heating temperatures were noted for motor vehicles operated in conditions of lack of roads, in travelling in columns and in pulling trailers, and when the vehicles were operated in mountainous locations.

The reduction in atmospheric pressure in a mountainous locale would seem to somewhat facilitate conditions for vapor lock formation. However, in addition to the pressure drop, the ambient air temperature also drops, and the results of conditions for vapor lock formation with increase in elevation change only very slightly.

Tests made of vehicles in chambers where tropical conditions were simulated, and in operating conditions -- in Central Asia, showed that the highest gasoline heating temperature (to 80-85° C) is observed after the vehicle has been stopped and the engine turned off. This is completely expected, since ventilation of the area under the hood stops, and the gasoline in the fuel system stops flowing and is strongly heated by the heat emitted from the engine. As a result, starting an engine even after a brief stop can be very difficult.

The tendency to an increase in power output and dimensions of modern engines, and an increase in the number of auxiliary instruments and devices with a simultaneous trend toward a reduction in the space under the hood considerably complicates the problem of removing the evolved heat. Tests made of the ZIL-11 passenger car in a tropical chamber showed that at an ambient air temperature of 35-40° C, the temperature of the feed pump housing reaches 105-115° C; when this happens, the gasoline can be heated to 75-85° C. This rise in temperature is caused by installing a layer of sound insulator under the hood in this vehicle, which also serves as a heat insulator.

The reduction in the gasoline heating temperature can be achived by very simple design measures. Measurements showed that even in new domestic motor vehicles, fuel pumps as a rule are installed in the hottest locations under the hood. Organizing good air ventilation near the fuel pump, heat insulation of the fuel pump, increasing the fuel system line diameters, and reducing fuel system line length and several other design measures promote a reduction in the gasoline heating temperature in the feed system.

Table 58. Dependence of gasoline temperature at which an engine stops due to vapor lock on the fractional composition of gasolines and gascline pump capacity

$t_{н.к.}$, °C 1	t_{10}, °C	$P_{н}$, мм рт. ст. 2	n	Температура бензина, °C, при которой глохнет двигатель, оборудованный насосами 3		
				Б-6 4	Б-9 5	Б-10 6
37	56	600	1000	55	64	74
			1600	47	55	61
34	48	647	1000	49	59	69
			1600	42	50	56
43	67	475	1000	66	75	85
			1600	59	67	72
44	67	462	1000	68	77	87
			1600	60	68	74
54	74	283	1000	86	95	102
			1600	78	87	90
53	75	268	1000	84	93	103
			1600	77	85	93
46	69	431	1000	70	80	89
			1600	63	71	77

Key:
1 -- $t_{i.b}$
2 -- P_{sat}, mm Hg
3 -- Temperature of gasoline, ° C, at which an engine equipped with the indicated pumps dries up
4 -- B-6
5 -- B-9
6 -- B-10

Based on the generalization of data from domestic and foreign investigations, it can be regarded as established that in hot climatic conditions, when an engine is being operated, gasoline temperature is 20-35° C higher than the ambient air temperature, and 7-10 minutes after a motor vehicle has been stopped and the engine turned off, it is 30-40° C higher. These values were used subsequently in calculations and justifications for requirements placed on the fractional composition of automotive gasolines.

When a comparison was made of gasoline having different fractional compositions in the fuel system of the same engine, the most appropriate criterion for rating the tendency of gasolines to form vapor locks is the gasoline temperature at which the engine dies due to vapor lock formation. To find these temperatures, experiments were made with a full-sized engine in stand conditions in which the gasoline was heated in the feed system [32]. The results (Fig. 75) showed that as the crankshaft rpm is increased, vapor

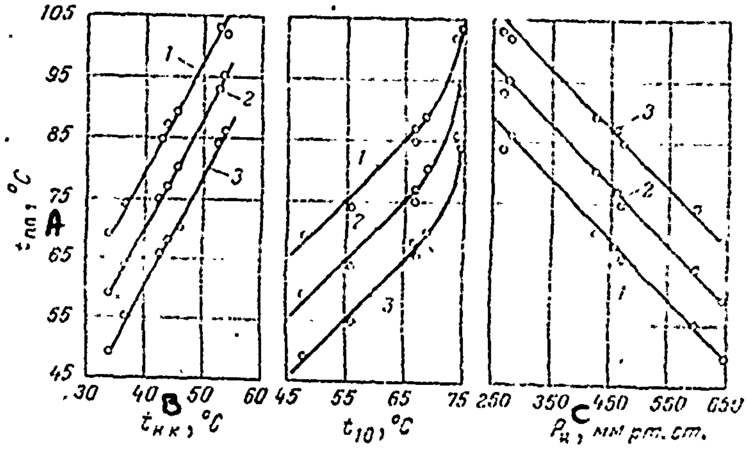

Fig. 76. Dependence of heating temperature of gasoline at which vapor locking develops on the fractional composition and saturated vapor pressure:

1 -- B-10 pump
2 -- B-9 pump
3 -- B-6 pump
Key: A -- $t_{v.l}$
B -- $t_{i.b}$
C -- P_{sat}, mm Hg

locks form at increasing the lower gasoline heating temperatures. Increasing the load on the engine also leads to the facilitation of vapor lock formation. The capacity of the feed pump changes only slightly with variation in the crankshaft rpm to 1000, while the required amount of gasoline steadily rises. It is precisely for this reason that as the rpm is increased, vapor lock formation begins at increasingly lower gasoline heating temperatures.

Analysis of domestic and foreign materials shows that the most "convenient" location for vapor lock formation is the fuel pump. Here gasoline acquires a fairly high temperature and (in the intake area) is at a minimum pressure. With flow toward the carburetor, the temperature of the gasoline rises somewhat, however vapor lock formation in this line is less probable owing to a slight excess pressure.

It must be noted that the fuel pump is also the "narrowest" place in domestic feed systems, restricting their handling capacity. When rating the vapor lock tendency of seven gasoline samples having different fractional compositions for engine with three fuel pumps [32] of different capacities (the B-6 pump with a capacity of 60-90 l/hr, the B-9 pump with a capacity of 150-175 l/hr, and the B-10 pump with the capacity of 185-210 l/hr), it was found (Table 58), that as the fuel pump capacity is increased, the gasoline temperature at which the engine stops due to vapor lock formation rises significantly. A pump with increased capacity is able to pump more vapor and therefore the engine continues to function normally at the higher gasoline temperature. Obviously, a rise in the fuel pump capacity is one of the possible and efficient ways of combatting the formation of vapor lock at elevated ambient air temperatures.

Investigations of seven different gasoline samples established the maximum gasoline heating temperatures at which an engine can stop due to vapor lock formation as a function of the initial boiling point, the 10 percent distillation point, and the saturated vapor pressure of the gasoline (Fig. 76). With increase in the initial boiling point of a gasoline, the temperature of the maximum allowable gasoline heating also rises linearly.

The dependence of the vapor lock formation temperature on the 10 percent gasoline distillation temperature (Fig. 76) is linear for gasolines that have a 10 percent distillation temperature in the limits 45-70° C, that is, for most modern automotive gasolines. When the 10 percent gasoline distillation temperature is higher than 70° C, the gasoline heating temperature up to vapor lock formation rises sharply. In this case, the transmissive capacity of the fuel system proves sufficient to ensure the trouble-free operation of the engine at high gasoline heating temperatures. The amount of vapor formed from these fuels is so small that the admission of the liquid phase completely satisfies fuel consumption for the given engine operating regime. The vapor lock formation temperature as a function of the gasoline saturated vapor pressure proved to be linear.

Based on these results, empirical functions were derived (Table 59) for the maximum gasoline heating temperature at which the engine stalls due to vapor lock formation ($t_{v.1}$), with dependent variables including gasoline saturated vapor pressure at 38° C and the fractional composition of the gasoline -- the initial boiling temperature ($t_{i.b}$) and the 10 percent distillation temperature (t_{10}).

<u>Rating methods</u>. The above-derived empirical dependences of the gasoline temperature at which the engine stops due to vapor lock formation on the indicators of fractional composition and saturated vapor pressure are only approximate in nature and are intended mainly to formulate the requirements pertaining to these indicators for seasonal and regional gasolines.

Actually, the initial gasoline boiling point, the 10 percent gasoline distillation temperature, as well as the gasoline saturated vapor pressure cannot characterize all processes occurring in vapor lock formation. The tendency of a gasoline to form vapor lock depends on the amount and properties of the hydrocarbons which at a given temperature and pressure are capable of passing from the liquid to the vapor state. Naturally, the lower the boiling point and the lower the 10 percent gasoline distillation

Table 59. Gasoline temperature at which an engine stops due to vapor lock ($t_{v.l}$) as empirical functions of the saturated vapor pressure (P_{sat}) and the gasoline fractional composition ($t_{i.b}$ and t_{10})

Насос 1	$t_{п.п.} = f(P_н)$ 2	$t_{п.п.} = f(t_{н.к.})$ 3	$t_{п.п.} = f(t_{10})$ 4
Б-6 5	$114 - 0,1P_н$	$1,85t_{н.к.} - 13$ 8	t_{10}
Б-9 6	$123 - 0,1P_н$	$1,85t_{н.к.} - 4$ 9	$t_{10} + 10$
Б-10 7	$133 - 0,1P_н$	$1,85t_{н.к.} + 5$ 10	$t_{10} + 20$

Key:
1 -- Pump
2 -- $t_{v.l} = f(P_{sat})$
3 -- $t_{v.l} = f(t_{i.b})$
4 -- $t_{v.l} = f(t_{10})$
5 -- B-6
6 -- B-9
7 -- B-10
8 -- $1.85\ t_{i.b} - 13$
9 -- $1.85\ t_{i.b} - 4$
10 -- $1.85\ t_{i.b} + 5$

temperature, and the higher its saturated vapor pressure, the higher is the fuel's tendency to vapor lock formation. But they cannot be a rigorous and definite quantitative relation between these indicators, since none of them characterizes how much vapor can form in the gasoline when it is heated. Therefore data on the fractional composition and saturated vapor pressure of a gasoline do not always permit a reliable rating of its tendency to vapor lock formation. Several empirical formulas and nomograms relating the tendency of a gasoline to vapor lock formation with its fractional composition and saturated vapor pressure have been proposed in the literature, but they all have only limited application and low precision.

In recent years foreign specialists, in conducting research work, are increasingly relating the vapor lock formation tendency of a gasoline to change in the ratio of vapor phase to liquid phase when a gasoline is heated. The foreign literature describes two methods of rating the ratio of the vapor phase to the liquid phase of gasoline at various temperatures [15, 17, 33-36]. Essentially, both methods amount to finding the temperature dependence of the vapor:liquid ratio when gasoline is heated in conditions of thermostating at a specific pressure. The methods differ in equipment and techniques.

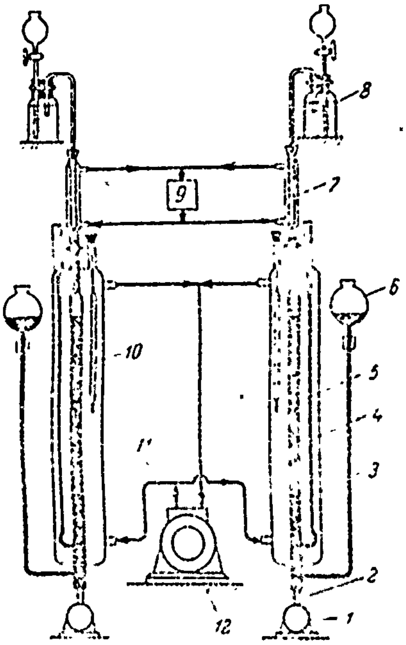

Fig. 77. Diagram of Sanburn Company instrument for determining the temperature dependence of the vapor-liquid ratio in automotive gasolines:

1 -- mixer drive
2 -- mixer
3 -- glass sleeve
4 -- leveling tube
5 -- calibrated buret
6 -- mercury flask
7 -- buret for pouring gasoline
8 -- sampler with siphon
9 -- thermostat
10 -- thermometer
11 -- tank for heating water
12 -- circulating pump

The first method was tested by the author in a laboratory and in the verification showed low precision and poor reproducibility for an overly long determination time. These drawbacks are a consequence of the equipment not ensuring effective mixing of the vapor and liquid phases of a gasoline. Evaporation and condensation in these conditions occurs slowly and the equilibrium between the phases is very difficult to attain. The second method of rating the ratio of the vapor to liquid phase of gasolines at different temperatures (the Sanburn method) was found to be much simpler, more precise, and more convenient and was subsequently used by us in rating the vapor lock formation tendency of gasolines.

The Sanburn instrument (Fig. 77) consists of two 100-ml thermostated burets 5, two paddle mixers 2 whose blades are enclosed within the entire length of the burets, and a circulating pump 12 ensuring thermostating. The vapor:liquid ratio was determined with the Sanburn instrument as follows.

The test gasoline cooled to 0° C was placed by a covered technique in the upper burets 7. Water cooled to 0° C in a special coil bath was continuously fed into the jackets of these burets. At the start of the experiment the burets 5 were filled with mercury using leveling flasks. Gasoline in the amount of 2 ml was pumped from burets 7 to burets 5 and the cock separating the burets was tightly closed. The mixers, circulating pump, and electric heating of the water in the tank were turned on, and the water in the jackets of burets 5 was heated. On attaining the required temperature and with a 5-minute exposure at this temperature, one notes the level of the vapor phase in burets 5. During the determination time the pressure level in the buret must be 760 mm Hg. For this purpose, using the leveling flask in a side branch tube the mercury level is found which when added to the atmospheric pressure yields 760 mm Hg. The dependence of the vapor-to-liquid phase ratio of gasoline on the gasoline heating temperature is plotted on the graph.

As a result of extensive tests [37-41], it was found that the maximum allowable vapor:liquid ratio is 25 for most foreign motor vehicles of the most diverse models. The maximum vapor:liquid ratio for fuel systems of domestic motor vehicles, as shown by the experiments, is also close to this value and is 25-30.

Using this ratio, we can establish the limiting relations between the gasoline heating temperature in the fuel system and the pressure which limit the range of operation without vapor lock formation when winter and summer automotive gasolines are used. Fig. 78 shows the ratio of the vapor phase to the liquid phase for winter and summer gasolines as functions of pressure for various temperatures. Based on these data, and assuming that the maximum phase ratio is 27.5, we can obtain the limiting relation between temperature and pressure in a system restricting the parameters of its operation without vapor lock formation (Fig. 79). These data permit a substantiated selection of hydraulic and temperature characteristics of automotive feed systems.

Effect of low-boiling components. The vapor lock formation tendency of gasolines when various low-boiling components are added was rated on a Sanburn instrument. Thermal cracking gasoline and platforming gasoline to which additions were made of butane (3.7 and 10 percent), natural gasoline

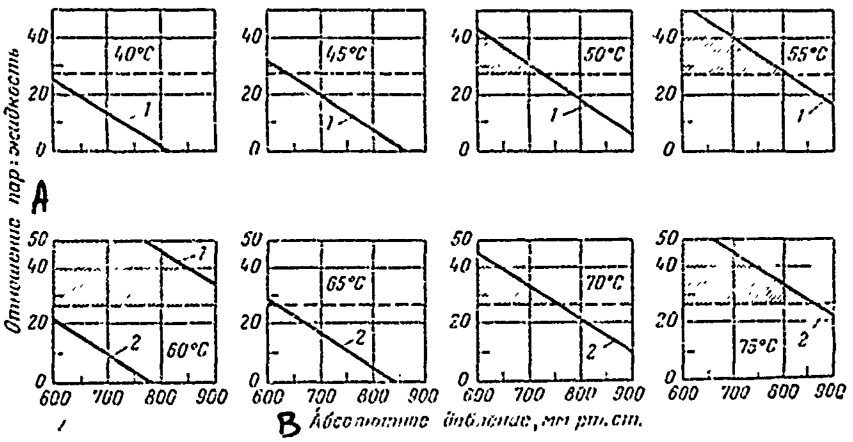

Fig. 78. Dependence of the air-liquid ratio of gasolines on pressure for various temperatures

1 -- winter gasoline

2 -- summer gasoline

Key: A -- Vapor/liquid ratio

B -- Absolute pressure, mm Hg

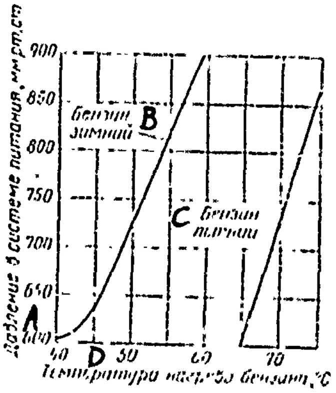

Fig. 79. Dependence of available pressure in feed system on heating temperature for various kinds of gasoline

Key: A -- Pressure in feed system, mm Hg

B -- Winter gasoline

C -- Summer gasoline

D -- Heating temperature of gasoline

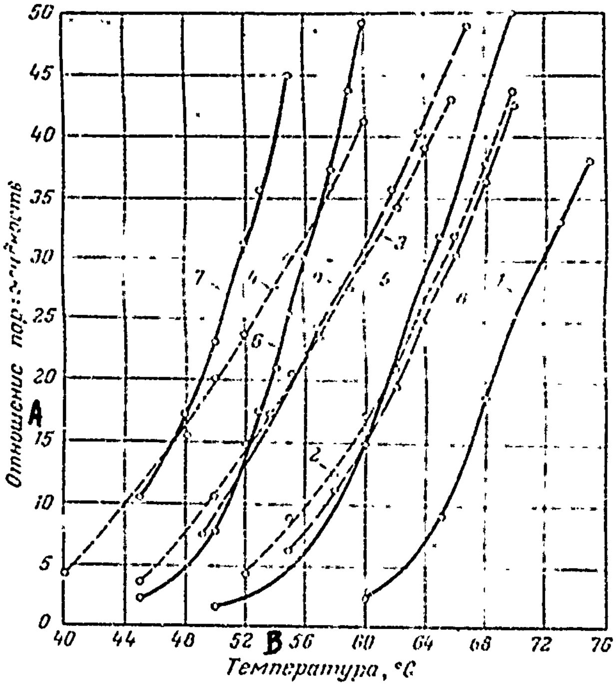

Fig. 80. Temperature dependence of vapor/liquid ratio of thermal cracking gasoline containing various components:

1 -- initial gasoline
2 -- as above + 3 percent butane
3 -- as above + 5 percent butane
4 -- as above + 10 percent butane
5 -- as above + 5 percent isopentane
6 -- as above + 10 percent isopentane
7 -- as above + 15 percent isopentane
8 -- as above + 5 percent natural gasoline
9 -- as above + 10 percent natural gasoline
Key: A -- Vapor/liquid ratio
B -- Temperature

(5, 10, and 15 percent), and technical isopentane (5, 10, and 15 percent) were studied. The resulting gasoline temperature dependences of the vapor: liquid ratio are shown in Fig. 80. The first thing that is striking when these data are analyzed is the change in the nature of the curves for gasolines containing isopentane. The temperature curve of the vapor:liquid ratio for gasolines containing isopentane is considerably steeper than for gasolines containing butane and natural gasoline.

Table 60. Comparison of vapor lock tendency of gasolines

Образец 1	$t_{п.п.}$, °C, определенная расчетным путем на основании значений 2			
	$t_{н.к.}$, °C 3	t_{10}, °C	$P_{н}$, мм рт. ст. 4	Отношение пар : жидкость 5
Бензин термического крекинга 6	85	77	79	70
с 3% бутана 7	64	70	66	64
с 7% бутана 8	53	65	56	58
с 10% бутана 9	50	62	51	53
с 5% газового бензина 10	72	68	65	64
с 10% газового бензина 11	51	63	56	58
с 15% газового бензина 12	53	58	52	—
с 5% изопентана 13	76	68	68	63
с 10% изопентана 14	64	63	60	55
с 15% изопентана 15	59	57	55	51
Бензин платформинга 16	66	65	59	56
с 3% бутана 7	57	60	52	50
с 7% бутана 8	52	56	46	45
с 10% бутана 9	42	53	44	39
с 5% газового бензина 10	59	60	53	50
с 10% газового бензина 11	53	55	49	45
с 15% газового бензина 12	50	53	48	—
с 5% изопентана 13	63	60	55	50
с 10% изопентана 14	57	56	52	46
с 15% изопентана 15	53	54	50	44

Key: 1 -- Sample
2 -- $t_{v.l}$, ° C, determined by calculation based on the indicated data
3 -- $t_{i.b}$
4 -- P_{sat}, mm Hg
5 -- Vapor/liquid ratio
6 -- Thermal cracking gasoline
7 -- +3 percent butane
8 -- +7 percent butane
9 -- +10 percent butane
10 -- +5 percent natural gasoline
11 -- +10 percent natural gasoline
12 -- +15 percent natural gasoline
13 -- +5 percent isopentane
14 -- +10 percent isobutane
15 -- +15 percent isobutane
16 -- Platforming gasoline

The curves in Fig. 80 show that from the standpoint of the vapor lock formation tendency, adding 3 percent butane is equivalent to adding 5 percent natural gasoline or isopentane, and adding 7 percent butane is equivalent to adding 10 percent natural gasoline or isopentane. The vapor lock formation tendency is higher in isopentane-containing gasoline and in gasoline containing the same amount of natural gasoline.

The best results in efforts to improve the starting qualities were obtained when butanes were added. However, adding butane quite sharply increases the vapor lock formation tendency of gasolines. To avoid vapor lock formation, the total butane content in gasolines must not exceed 10 percent.

A comparison of natural gasoline and isopentane revealed that from the standpoint of improving the fractional composition of commercial automotive gasolines, natural gasoline is more effective. Earlier it was shown that adding natural gasoline has a greater effect on improving the starting qualities of gasoline by adding the same amount of isopentane. A similar result was found in rating the tendency of gasolines to form vapor locks: in the presence of isopentane the danger of vapor locks appearing is higher than in the presence of the same amount of natural gasoline. Thus, in producing commercial gasolines it must be taken into account that natural gasolines are preferable in improving fractional composition. Isopentane is more preferable to use as a low-boiling component when it is necessary to raise the fuel octane number.

Table 60 presents data on the tendency of gasolines containing various components to form vapor locks, when this property is rated by various indicators. All the quantities in the table were obtained by calculation using formulas for a motor vehicle with a B-9 fuel pump.

The results show that the temperature of a gasoline at which vapor locks form, predicted on the basis of data dealing with fractional composition and saturated vapor pressure, can differ widely from the temperature determined on the basis of the vapor:liquid phase ratio.

Seasonal and Regional Gasolines

The enormous extent of our country's territory is responsible for the diversity of climatic conditions. The USSR has all the main types of climates in the world. Large expanses of our country lie in the arctic circle. These areas are characterized by prolonged and severe winters, sometimes with strong winds. Part of the territory in the temperate zone is occupied by zones of semideserts and deserts with continental, extremely arid climate and very hot summers. The general property of the climate in the temperate zone of the USSR is a well-defined delineation between the cold and warm periods of the year. The contrast between winter and summer,

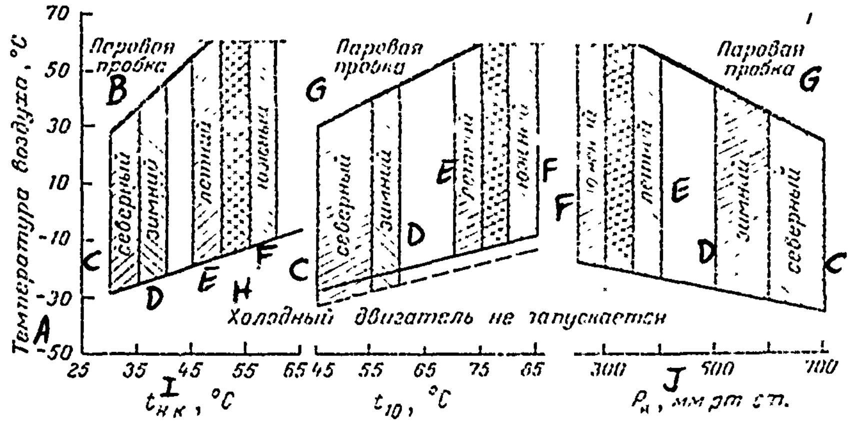

Fig. 81. Temperature limits of the efficiency of automotive engines as a function of gasoline fractional composition and saturated vapor pressure

Key: A -- Air temperature
B -- Vapor lock
C -- northern
D -- winter
E -- summer
F -- southern
G -- Vapor lock
H -- Cold engine does not start
I -- $t_{i.b}$
J -- P_{sat}, mm Hg

the duration of the seasons, and the very nature of the seasons can differ, but are still quite well-defined. Thus, climatic conditions of the USSR are such that the general use of gasolines having the same fractional composition at any time of the year inevitably involves increased fuel consumption, longer engine starting times, reduced engine reliability, reduced engine longevity, and so on.

Results of studies which have been discussed in the preceding two sections made it possible to find the starting qualities of gasolines and their vapor lock tendency as functions of the fractional composition and saturated vapor pressure of gasolines. Based on these functions we can establish temperature limits to the efficiency of automotive engines restricted by gasoline fractional composition (Fig. 81).

To most fully satisfy engine requirements with allowances for the climatic characteristics of the USSR, automotive gasolines must be subdivided by their fractional composition into two regional and two seasonal

Table 61. Requirements on fractional composition of seasonal and regional automotive gasolines

Сорт бензина 1	$t_{н.к.}$, °C 2	t_{10}, °C	$P_{н}$, мм рт. ст. 3	$t_{в}$, °C 4	$t_{н.п.}$, °C 5
Северный 6	10 Не>35	10 Не>55	11 Не<600 10 Не>700	−30	+30
Зимний 7	10 Не>40	10 Не>60	11 Не<500 10 Не>600	−25	+35
Летний 8	11 Не<45	11 Не<70 10 Не>80	11 Не<300 10 Не>400	−15	+50
Южный 9	11 Не<50	11 Не<75 10 Не>85	11 Не<250 10 Не>350	−10	+55

Key: 1 -- Grade of gasoline
2 -- $t_{i.b}$
3 -- P_{sat}, mm Hg
4 -- t_a
5 -- $t_{v.l}$
6 -- Northern
7 -- Winter
8 -- Summer
9 -- Sothern
10 -- Not more than
11 -- Not less than

grades [42]. Supplying fuels to remote regions, especially in the north of our country, involves certain difficulties, therefore gasolines for the northern and southern regions must be all-seasonal. The following classification of gasolines by fractional composition is justified on a technical basis [42].

All-seasonal northern gasoline is intended for use in regions lying northward and northeastward of the −20° C January isotherm. The gasoline must ensure cold engine starts when the air temperature is −30° C and at the same time not cause vapor lock formation in conditions of summer use of motor vehicles when the air temperature may be up to +30° C.

All-seasonal southern gasoline is used in the southern regions of the country situated south of the +25° C July isotherm. The main requirement on this gasoline is the absence of vapor locks in the feed system when the air temperature is up to +55° C. The gasoline must ensure cold engine starts in the winter when the air temperature is down to −10° C.

Summer and winter gasolines are intended for use in the central belt of the country. Winter gasoline must ensure cold engine starts when the air temperatures are down to -25° C and the absence of vapor locks when the air temperature is +35° C; summer gasoline must likewise ensure starts down to -15° C and the absence of vapor lock at temperatures up to +50° C. These grades of automotive gasolines must have the following fractional composition indicators (Table 61).

Automotive gasolines having the indicated fractional composition will most fully satisfy engine requirements in various climatic conditions of service and their use must provide considerable savings. However, considering the inevitable difficulties involved in producing and shipping gasolines of different fractional compositions, especially at those refineries that produce gasolines for use in different climatic zones, a gradual conversion to producing regional and seasonal automotive gasolines is possible. In the first stage, two gasolines differing in fractional compositions -- winter and summer -- must be provided for in production for a certain length of time. During this period winter gasoline must be used both as all-seasonal northern gasoline, and summer gasoline -- also as an all-seasonal southern gasoline. Precisely this intermediate step was then made with the issuance of GOST 2084-67 which provides for producing automotive gasolines of the winter and summer kinds.

To confirm the validity of the above-presented principles and the requirements on fractional composition, experimental batches of the various gasolines were produced, investigated, and tested (Table 62).

Fig. 82 presents data on the changes in the saturated vapor pressure of all the tested gasolines as a function of temperature. It must be noted that the saturated vapor pressure of northern gasoline decreases less sharply with a temperature drop than the saturated vapor pressure of other gasolines. This is accounted for the presence in northern gasoline of more than 5 percent butanes.

When the temperature dependence of gasoline saturated vapor pressure was plotted in semilogarithmic coordinates (Fig. 82), a characteristic regularity was found, which is that with increasing heaviness of the fractional composition of gasolines, the curves $\lg p = t(1/T)$ becomes deeper, that is, at low temperatures the relative difference between the gasolines becomes much greater. These data once again indicate that the slope of the curves depends on the amount and composition of the low-boiling components. The difference in the saturated vapor pressure as between northern and other gasolines rises with decrease in temperature.

For the laboratory rating of the vapor lock tendency of northern gasoline, the temperature dependence of the vapor-to-liquid phase ratio was determined on the Sanburn instrument. The data (Fig. 83) show that the vapor-to-liquid ratio of 25-30 (ensuring trouble-free engine operation) is attained when the northern gasoline grade is heated to 51-55° C.

Table 62. Physicochemical indicators of gasolines tested

Показатель 1	Бензин А-76 северный 2		Бензин типа АИ-93 летний 5	Бензин А-76 летний (ГОСТ 2081—56) 6	Бензин А-76 южный 7
	образец 1 3	образец 2 4			
ОЧИМ 8	81,2	80,7	95,0	81,6	80,2
ОЧММ 9	77,4	76,9	87,0	76,5	76,0
Фракционный состав, °С 10					
$t_{н.к.}$ 11	30	32	38	46	68
t_{10}	53	53	74	63	80
t_{50}	90	91	110	103	101
t_{90}	142	142	134	162	141
$t_{к.к.}$ 12	170	167	159	139	171
Выход фракции, % 13	97,0	97,0	97,0	98,0	97,5
$P_н$	650	615	390	430	250
Кислотность, мг КОН/100 мл 14	0,1	0,2	0,1	0,1	0,2
Содержание фактических смол, мг/100 мл 15	4,0	3,6	1,8	4,6	5,2
Индукционный период, мин 16	800	800	600	480	480
Содержание серы, % 17	0,05	0,001	—	0,075	0,001
Углеводородный состав, % 18					
парафиновых и нафтеновых	63,8	65,0	64,8	62,0	60,5
ароматических 20 19	36,7	32,5	35,2	26,7	38,9
непредельных 21	0,0	2,5	0,0	11,3	0,6

Remark: The gasolines do not contain TEL and have a freezing point below -50° C.

Key:
1 -- Indicator
2 -- Northern A-76 gasoline
3 -- sample 1
4 -- sample 2
5 -- Summer AI-93 gasoline
6 -- Summer A-76 gasoline (GOST 2084-56)
7 -- Southern A-76 gasoline
8 -- ONIM
9 -- ONMM
10 -- Fractional composition
11 -- $t_{i.b}$
12 -- $t_{e.b}$
13 -- Fractional yield
14 -- Acidity, mg KOH/100 ml
15 -- Existent gum, mg/100 ml
16 -- Induction period, min
17 -- Sulfur content
18 -- Hydrocarbon composition
19 -- paraffinic and naphthenic
20 -- aromatic
21 -- unsaturated

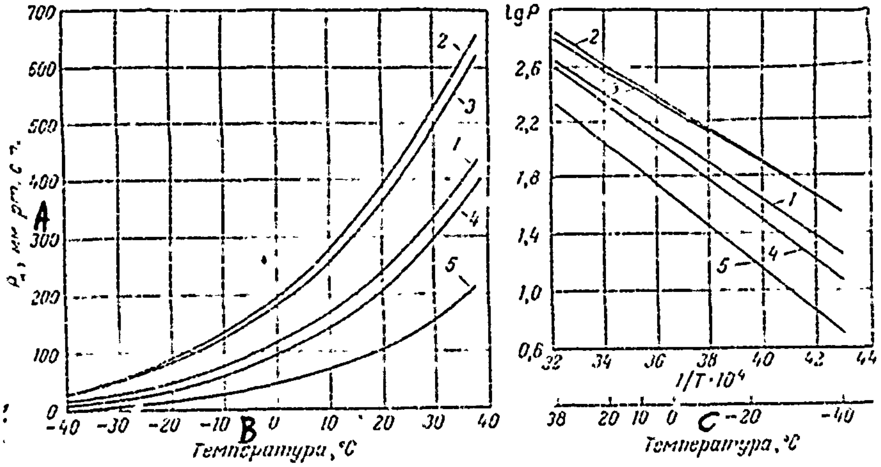

Fig. 82. Temperature dependence of saturated vapor pressure of test gasolines:

1 -- A-76 gasoline (GOST 2084-56)
2 -- northern A-76 gasoline, sample 1
3 -- northern A-76 gasoline, sample 2
4 -- summer AI-93 gasoline
5 -- southern A-76 gasoline

Key: A -- P_{sat}, mm Hg
B -- Temperature
C -- Temperature

The starting qualities of gasolines were rated by determining the minimum starting rpm for a ZIL-130 engine in a refrigerator chamber and by finding the minimum temperatures of the reliable start and the possible start. Tests show that the northern grade of A-76 automotive gasoline ensures a reliable start using ASZp-6 oil down to -28° C, and a possible start -- down to -32° C (Table 63).

Experiments in the refrigeration chamber revealed that compared with the earlier produced gasolines, use of the northern grade ensures a considerable reduction in the minimum starting rpm, especially at temperatures of -25° C and lower. For example, at -32° C use of the northern gasoline ensures a reduction in the minimum starting rpm from 40-42 rpm down to 22-24 rpm, and at -35° C, from 62-64 rpm down to 36-38 rpm, that is, by nearly half (Fig. 84).

The refrigeration chamber tests showed that when an engine crackshaft is idled at a speed exceeding the minimum rpm, starting of the engine using northern gasolines occurs much faster. The time required to start an engine is reduced by roughly half; here the period of time from the

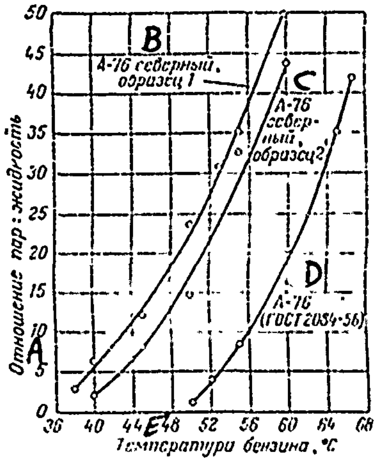

Fig. 83. Temperature dependence of vapor/liquid ratio for test gasolines
Key: A -- Vapor/liquid ratio
B -- Northern A-76, sample 1
C -- Northern A-76, sample 2
D -- A-76 (GOST 2084-56)
E -- Gasoline temperature

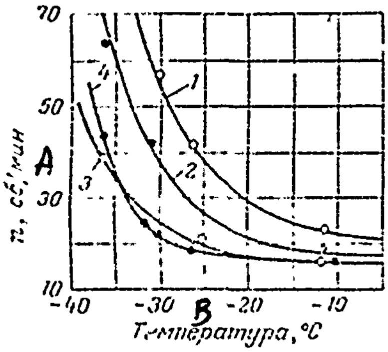

Fig. 84. Temperature dependence of minimum rpm of ZIL-130 engine when various kinds of gasoline are used:
1 -- AI-93 gasoline
2 -- A-76 gasoline (GOST 2084-56)
3 -- northern A-76 gasoline, sample 1
4 -- northern A-76 gasoline, sample 2
Key: A -- rpm
B -- Temperature

appearance of the first spark to the beginning of stable engine operation is also reduced. This latter fact ensures a reduction in the starting wear in engine parts.

Use of northern gasolines not only extends the limits to the possible cold engine starts, but also increases starting reliability at low temperatures. Tests revealed that at -15, -20, and -25° C nearly in every case a cold engine run on northern gasoline almost always starts from the first try, while it takes the second and third tries for other gasolines. The reduction in the number of tries leads to lesser gasoline consumption in starting and reduces starting wear of engine parts.

Use of the southern grade of A-76 gasoline ensures a reliable start for the ZIL-130 engine at temperatures down to -10° C. These data confirm the correctness of the requirements placed on the quality of the southern grade of this automotive gasoline.

Table 63. Possibilities of cold engine start when various fuels and oils are used

1 Двигатель	Масло 2	3 Температура, °С	
		надежного пуска 4	возможного пуска 5
	6 Бензин А-76		
ГАЗ-66 7	АС-8 9	—15	—20
	АСЗп-6 10	—19	—27
ЗИЛ-130 8	АС-8 11	—20	—24
	АСЗп-6 12	—24	—27
	13 Бензин А-76 (северный)		
ГАЗ-66 7	АС-8 9	—18	—22
	АСЗп-6 10	—25	—32
ЗИЛ-130 8	АС-8 11	—24	—26
	АСЗп-6 12	—28	—32

Key: 1 -- Engine
2 -- Oil
3 -- Temperature
4 -- reliable start
5 -- possible start
6 -- A-76 gasoline
7 -- GAZ-66
8 -- ZIL-130
9 -- AS-8
10 -- ASZp-6
11 -- AS-8
12 -- ASZp-6
13 -- A-76 gasoline (northern)

Tests made of northern gasoline dealing with its vapor lock tendency were conducted in stand conditions in a tropical chamber with racing drums and in operating conditions in the ZIL-130 vehicle during the summer. Vapor lock was observed to form in the conditions of the very severe tropical chamber tests for northern gasoline when the air temperature was 27-29° C.

Road tests made of northern gasoline were conducted at air temperatures to 35° C in two travel regimes -- free and specified. The free travel regime consisted of the ordinary operating regime which was carried out at the driver's discretion. The specified regime consisted in travelling at constant, "assigned" speeds (30, 50, and 80-90 km/hr). The road tests establish that no vapor locks form in the feed system in the free travel regime when northern gasoline is used and the air temperature is 35° C.

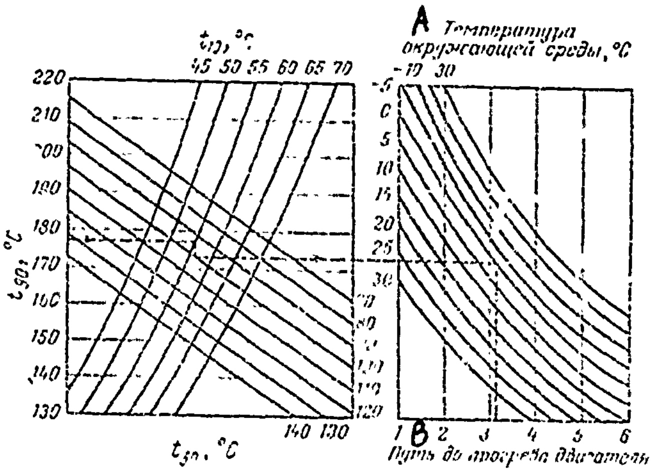

Fig. 85. Determination of path along which engine warm-up is achieved as a function of fractional composition of gasoline (nomogram)
Key: A -- Ambient temperature
B -- trip to engine warm-up, km

For travel in the specified regime, especially in low gear, the engine considerably overheated and produced unfavorable conditions for vapor lock formation. The locks disappear quite rapidly when the operating regime was changed. The lifetime of the vapor locks for operation using northern gasoline was 35-53 sec. The temperature of the gasoline at the carburetor inlet at which vapor locks formed was 54° C for the northern gasoline and 60° C for A-76 gasoline (GOST 2084-56). These data agree well with the data of laboratory studies estimating the vapor lock tendency of gasolines using the Sanburn instrument (Fig. 83). Based on the laboratory data on the vapor-liquid phase ratio, the maximum heating temperature before vapor lock formation was estimated in the range 51-55° C for the northern gasoline, and 62-63° C for A-76 gasoline (GOST 2084-56). As a result of determinations made in the road tests, these temperatures were found to be 54 and 60° C, respectively. Considering the actual motor vehicle operating conditions in which the engine temperature regime is much lower than that adopted in the stand and road tests based on the assigned regime, it can be held that the northern gasoline ensures normal vehicle operation at ambient air temperatures to 30-35° C.

Other Operating Indicators

<u>Engine warm-up and response</u>. Engine warm-up covers the time from starting of the engine until smooth stable operation is attained. The faster an engine warms up, the lower are the nonproductive time and gasoline outlays, and the less is the wear of engine parts. The warm-up rate

depends strongly on the gasoline fractional composition. If gasoline does not correspond to engine requirements in fractional composition, the warm-up time is increased and engine operation is accompanied by jerking. Sometimes an engine dies during the warm-up time.

Studies made indicate that the engine warm-up time depends mainly on the boiling point of the middle gasoline fractions. Virtually all investigators have reached this conclusion. However, in many studies effect of head and tail fractions on warm-up has been noted. The effect of these fractions is expressed, evidently, during different warm-up periods. In the initial period the amount of head fractions is significant, while at the end of their warm-up the presence of tail fractions is evident. Moreover, the gasoline tail fractions strongly affect warm-up characteristics if a gasoline with a high central fraction boiling point is used when the ambient air temperature is relatively low.

A function was derived [43] relating the temperatures for 10 percent, 50 percent, and 90 percent fuel distillation with the distance travelled until the engine warms up for various ambient air temperatures (Fig. 85). There is a nomogram for determining the warm-up time based on the 50 percent gasoline distillation temperature and the amount of gasoline evaporating to 70° C (Fig. 86). In this nomogram the role of the tail fractions in the warm-up process of the engine is not considered, since the data of numerous studies showed that the 90 percent distillation temperature has a clear effect on warm-up. Thus, two fuels differing only in the 90 percent distillation temperature (153 and 182° C) caused a 3 minutes difference in the warm-up time at -1° C and up to a 22 minutes difference in the warm-up time at -18° C.

The concept of "incomplete value", characterizing a given fuel compared with an "ideal" fuel was introduced for a quantitative expression on the data dealing with the effect of fractional composition on engine warm-up. The scale of incomplete value is equal to the difference in the acceleration velocities (in km/hr) for the test and the ideal fuel under strictly specific conditions. The higher the scale reading, the poorer the fuel. Studies showed that the incomplete value of fuel changes only slightly with variation in the 10 percent and 90 percent gasoline distillation temperatures and deteriorates markedly when the 50 percent gasoline distillation temperature is increased. The nature of the variation in incomplete value as a function of the 50 percent gasoline distillation temperature suggests that there is an optimal 50 percent gasoline distillation temperature, below which this indicator ceases to influence engine warm-up.

Naturally, the optimal 50 percent gasoline distillation temperature depends on the air temperature to which the engine warms up. As the air temperature is reduced, a lower 50 percent gasoline distillation temperature is necessary.

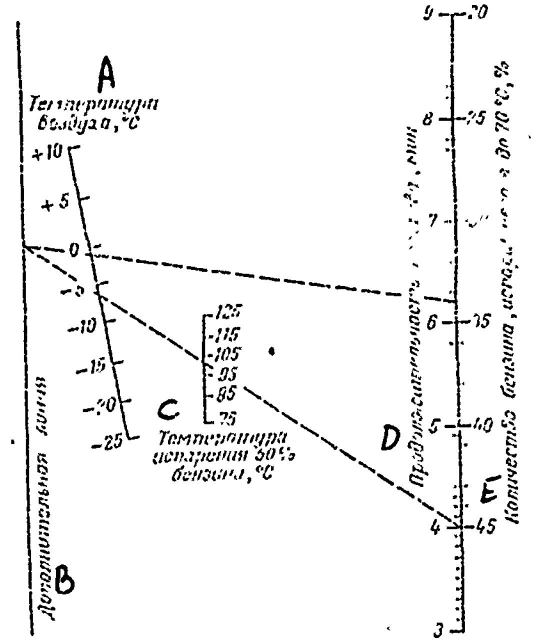

Fig. 86. Dependence of engine warm-up time on gasoline volatility and their temperature (nomogram)

Key: A -- Air temperature
B -- Supplementary line
C -- 50 percent gasoline vaporization temperature
D -- Warm-up time, min
E -- Amount of gasoline vaporizing to 70° C

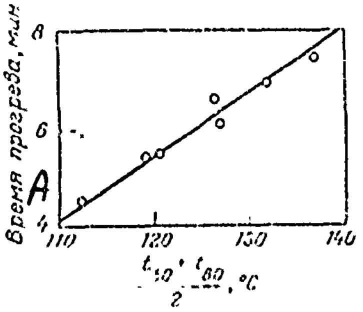

Fig. 87. Dependence of engine warm-up time on fuel volatility (speed 35 km/hr and air temperature 0° C)

Key: A -- Warm-up time, minutes

To estimate the effect of fractional composition on engine warm-up, various investigators characterize the middle fractions not only by the 50 percent gasoline distillation temperature. A linear dependence of the engine warm-up time on the half-sum of the 50 percent and 80 percent fuel distillation temperatures (Fig. 87) was found [14]. The warm-up time was also found to depend on the 65 percent gasoline distillation temperature, and on the slope of the distillation curve in the interval from 40 to 90 percent, and so on [15]. A critical examination of published results affords the recommendation of the following requirements for the 50 percent distillation temperature for seasonal and regional gasolines for domestic automotive engines (before special studies are conducted): not higher than 90° C for northern gasoline; not higher than 100° C for winter gasoline; not higher than 110° C for summer gasoline; and not higher than 120° C for southern gasoline.

Very similar requirements are imposed on gasoline fractional composition to ensure good engine response. By engine response we mean its ability to rapidly develop the required velocity (rpm) after the throttle has been sharply turned on. Engine response depends on gasoline fractional composition (mainly on the 50 percent distillation temperature) and the design characteristics of the carburetor and the engine intake system. The optimal acceleration is achieved if the volatility of the fuel ensures a mixture of air and fuel vapor in a 12:1 ratio. If the gasoline has poor volatility, then leaner mixtures are formed having compositions of 16:1, 18:1, and 20:1; in this event, as experiments showed, the acceleration time is increased by 9, 37, and 170 percent, respectively.

An investigation was made of the effect that the 50 percent gasoline distillation temperature has on acceleration characteristics at various air temperatures (Fig. 88) [15]. Varying the 50 percent distillation temperature within fairly wide limits had no marked effect on acceleration characteristics at an air temperature of 16° C. As the air temperature was reduced, the effect of the 50 percent fuel distillation temperature becomes progressively stronger. Even when the ambient air temperature is -1° C, the ability to accelerate is reduced by about 1 percent for each 5.6° C rise in the 50 percent gasoline distillation temperature.

A system was developed to estimating the relative acceleration characteristics of an engine as a function of gasoline fractional compositions based on the use of a special diagram [15]. However, this system has limited application. A study of the effect that the fractional composition of domestic gasolines has on the response of the GAZ-51 engine (Table 64) showed that even without a load on the engine, the amount of the middle and tail fractions in the gasoline significantly affect engine response.

The results of studies showed by foreign workers showed that the requirements on the 50 percent gasoline distillation temperature that are dictated by engine warm-up also provide for faster engine response.

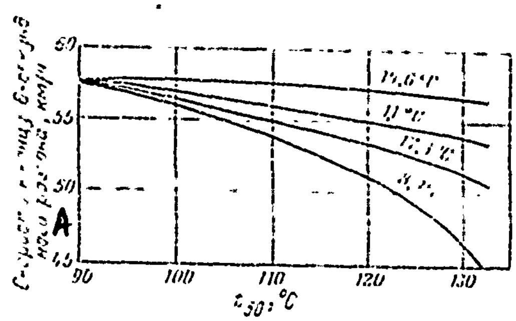

Fig. 88. Effect of fuel volatility on acceleration characteristic from 32 km/hr; the engine is warmed up with open manual-controlled throttle; t_{10} = 48-51° C, and the ambient air temperature is indicated next to the lines.

Key: A -- Velocity at end of 6-second acceleration, km/hr

Table 64. Effect of fractional composition of gasoline on the response of a nonloaded GAZ-51 engine

Время испытания, сек 1	2 Суммарное значение n (об/мин) после открытия дроссельной заслонки для работы на бензинах со следующими характеристиками				
	t_{50} = 97° C 3 $t_{к.к.}$ = 171° C	t_{50} = 107° C 3 $t_{к.к.}$ = 175° C	t_{50} = 112° C 3 $t_{к.к.}$ = 180° C	t_{50} = 120° C 3 $t_{к.к.}$ = 182° C	t_{50} = 124° C 3 $t_{к.к.}$ = 186° C
1/8	9,0	9,0	8,0	7,0	7,0
2/8	23,5	23,0	20,5	18,5	19,5
3/8	44,0	41,0	40,0	38,0	36,5
4/8	70,0	68,0	66,0	60,5	59,5
5/8	100,0	100,0	95,5	88,5	86,5
6/8	136,0	142,0	131,0	130,5	120,0
7/8	176,5	172,0	165,5	162,0	159,5
8/8	221,0	[illegible]	211,5	203,5	200.0

Key: 1 -- Test time, seconds
2 -- Overall value of n (rpm) after throttle was opened for operation with gasolines having the following characteristics
3 -- $t_{e.b}$

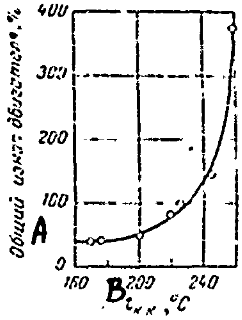

Fig. 89. Effect of gasoline end boiling point on engine wear
Key: A -- Total engine wear
B -- $t_{e.b}$

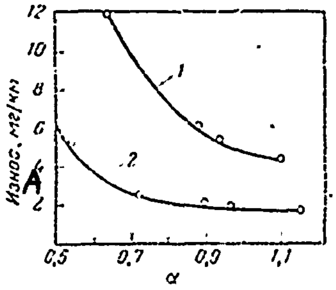

Fig. 90. Dependence of engine wear on fractional composition of fuel and combustible mixture, composition [24]:
1 -- gasoline with $t_{e.b} = 225°$ C and $t_{90} = 200°$ C
2 -- gasoline with $t_{e.b} = 205°$ C and $t_{90} = 180°$ C
Key: A -- Wear, mg/km

Engine wear and operating economy. Total evaporation of gasoline in an engine is characterized by the 90 percent distillation temperature and by the end boiling point. When these values are high, the heavy gasoline fractions do not evaporate in the engine intake manifold and enter the cylinders in liquid form. The liquid portion of the gasoline does not completely evaporate in the combustion chamber and the unevaporated portion flows through the piston ring gaps into the engine crankcase. And the oil is washed off the cylinder walls and is diluted in the crankcase.

N. V. Brusyantsev [44] found that generally speaking the gasoline fractions boiling above 180° C enter the crankcase oil and that the viscosity of the lubricating oil is somewhat reduced. However, the main reason for the rapid wear of automotive engines when fuels with poor volatility are used is not the dilution of crankcase oil but the washing off of oil from rubbing parts by the unevaporated fuel: semidry friction of parts occurs in the areas where the oil has been washed off, accompanied by increased wear [45]. Dilution of oil in the crankcase indicates only that oil is being washed off in the engine, causing increased wear.

An engine operating in the cold time of the year on heavy fractional-composition gasolines wears out especially intensively. And in this case the increased wear is a consequence of the oil film being washed off from the cylinder walls and not of oil being diluted in the crankcase. Incidentally, the gasoline entering the oil quite rapidly evaporates as the engine runs and the oil viscosity is restored:

	Gasoline content in oil, percent	ν_{50}, cst
Fresh oil	0.0	41.0
Oil diluted with gasoline	10.0	17.5
Oil circulating in an engine for		
5 minutes	7.5	19.0
10 minutes	6.4	20.6
30 minutes	3.5	25.9
60 minutes	1.9	32.0
24 hours	0.8	35.7
Spent oil*	--	35 - 38

* operating data.

A relationship between the end boiling point of gasoline used and total engine wear is shown in Fig. 89. The very abrupt rise in wear as the end boiling point of automotive gasolines is increased is striking.

The effect of gasoline fractional composition on engine wear also depends on mixture composition (Fig. 90). The difference in fractional composition proves to be more intense for rich mixtures.

When gasolines with high end boiling point are used, besides greater wear higher fuel consumption is observed (Fig. 91), the nonuniformity of combustible mixture distribution by engine cylinder is intensified, and the gasoline's tendency to deposit formation is increased.

Thus, a reduction in the end boiling point of gasoline and thus in the 90 percent gasoline distillation temperature improves a good many operating properties, but in so doing the reserves of automotive gasoline are appreciably reduced. In our country the quality of commercial automotive gasolines has been systematically improved by lowering the end boiling point. During the Great Patriotic War automotive gasoline was produced with an end boiling point of 235° C (GOST V2084-43), and then petroleum refineries converted to producing gasoline with an end boiling point of 225° C, and from 1946 the end boiling point of gasolines was lowered down to 205° C (GOST 2084-46), and since 1967 down to 195° C (for summer grades) and down to 185° C (for winter grades) for the gasolines A-72, A-76, AI-93, and AI-98.

Selection of optimal end boiling points and 90 percent distillation temperatures for commercial gasolines at the present time takes on particular added emergency due to the wide introduction of catalytic reforming gasolines. When gasoline fractions undergo catalytic reforming, as the result of the aromatization of the end product the end boiling point of gasoline rises significantly. And in contrast to straight-run and thermal cracking gasolines,

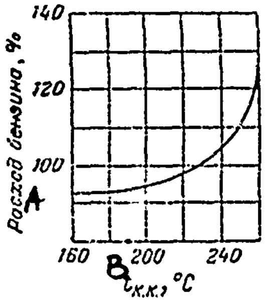

Fig. 91. Effect of end boiling point of gasoline on its consumption in the operation of automotive vehicle
Key: A -- Gasoline consumption
B -- $t_{e.b}$

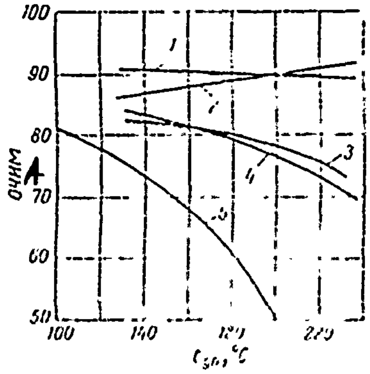

Fig. 92. Effect of 90 percent gasoline distillation temperature on the octane number of gasolines of various origins:
1 -- catalytic cracking
2 -- catalytic reforming
3 -- thermal reforming
4 -- thermal cracking
5 -- straight-run
Key: A -- ONRM

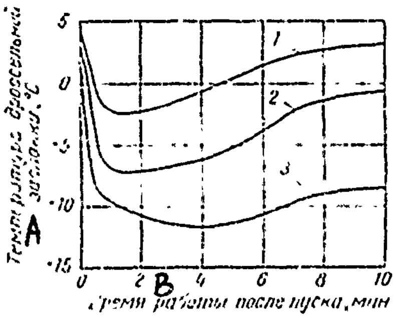

Fig. 93. Fuel volatility and cooling of metal parts of carburetor:
1 -- fuel with low volatility
2 -- fuel with moderate volatility
3 -- fuel with high volatility
Key: A -- Throttle temperature
B -- Operating time after starting, minutes

the highest octane hydrocarbons are precisely in the tail fractions of reforming gasolines (Fig. 92). Lowering the end boiling point of reforming gasolines worsens their knock resistance, thus, optimal end boiling point and 90 percent distillation temperatures must be found anew for domestic commercial gasolines containing catalytic reforming components. Research and economic calculations are needed to solve this question. It must be noted that at the present time automotive gasolines with end boiling point of 215-220° C are being produced and used in foreign practice in a good many countries [46].

Idling operation of an engine. Difficulties in starting a warmed engine can be observed in the repeated starting of an engine that has been stopped after prolonged operation with high load. When an engine is stopped, the ventilation of the space under the hood ceases the carburetor can heat up to very high temperatures due to the irradiation of heat from the engine. When this happens, the gasoline will evaporate in the float chamber and channels of the carburetor. Further, depending on the carburetor design, gasoline vapor will collect in the carburetor and force liquid gasoline into the intake manifold or else the gasoline vapor will enter the mixing chamber of the carburetor and the intake system, or directly into the atmosphere.

When liquid is forced into the intake system of an engine (this phenomenon is called "percolation"), an overrich mixture is produced and normal carburetor operation becomes impossible. In the event gasoline evaporates into the mixing chamber or into the atmosphere, the fuel level in the float chamber drops and the engine can be started only after the fuel pump has fed the required amount of gasoline.

Until recently, removing the gasoline vapor formed into the atmosphere was held to be the most effective solution to this problem. However, in recent years owing to the need to clean air basins over cities, the methods of solving this problem have been under re-examination, since atmospheric contamination is unacceptable.

The unsatisfactory operation of a warm engine in idling is also associated with the evaporation of gasoline, when for a small gasoline consumption and a low rate of gasoline pumping into the fuel system the gasoline temperature rises. This phenomenon is especially dangerous in hot weather after an engine has been run with full load (during travel time or in brief stops). As a result of some of the gasoline evaporating in these conditions, an overrich working mixture can be formed, which leads to uneven idling and, in extreme cases, to engine stoppage due to the "flooding" of the carburetor because of gasoline "percolation".

Difficulties of a warm start and operation of an engine in idling are associated with the same gasoline qualities responsible for the gasoline tendency to form vapor locks. Experience showed that the formation of vapor locks is the most important and determining problem associated with the evaporation of gasoline in the engine fuel system. It was found that gasoline that ensures the absence of vapor locks cannot cause difficulties in the starting of a warm engine or during operation of an engine in idling.

Carburetor icing. The evaporation of gasoline in an engine intake system is accompanied by a lowering of the fuel-air mixture temperature because the heat required to evaporate the gasoline (heat of vaporization) is abstracted from the air in which the evaporation occurs and from the metal parts of the intake system. For example, it was noted that at an ambient air temperature of 7.5° C the temperature of the throttle drops to -14° C 2 minutes after the engine has been started. Studies showed that the temperature drop in the engine intake system depends on gasoline volatility (Fig. 93).

Owing to the drop in the air-fuel mixture temperature, the moisture presence in the air condenses on the cold parts of the intake system forming crusts of ice. Ice formation on the jet nozzles disrupts normal streaming of gasoline, leans the combustible mixture, and leads to a reduction in crankshaft rpm.

Icing of the venturi can occur in some engines. This phenomenon is usually observed in the steady operation of an engine at high rpm in cold wet weather. Ice formation on venturi walls reduces its cross-section and intensifies the rarefaction, and thus increases gasoline consumption. The excessive enrichment of the mixture leads to a drop in engine power and higher specific fuel consumption. The extent of carburetor icing depends on air temperature and humidity, the design of the intake system, gasoline volatility, and the latent heat of vaporization of the components in the gasoline.

The most favorable conditions for carburetor icing are produced on a cold damp day, or during rain or fog (Fig. 94). The largest number of misfires in engine operation due to carburetor icing is observed at 100 percent relative humidity and at an ambient air temperature of about 4.5° C. A temperature of 11° C is too high for carburetor icing, while at a temperature below -2° C even in saturated air there may be too little moisture to cause carburetor icing. Favorable conditions for this are most often produced in areas with strongly pronounced maritime climate.

When easily evaporated fuels are used, their nearly total evaporation ends in the carburetor, and therefore it is cold faster and ices more often and in a broader range of temperatures and relative humidities. Studies showed that in all cases a rise in the 10 percent, 50 percent, and 90 percent gasoline distillation temperatures reduces carburetor icing. The greatest effect comes from a rise in the 10 percent gasoline distillation temperature, and the least effect stems from the 90 percent gasoline distillation temperature. Preventing carburetor icing by increasing the 10 percent gasoline distillation temperature is not used since this worsens the starting qualities of the gasoline [15].

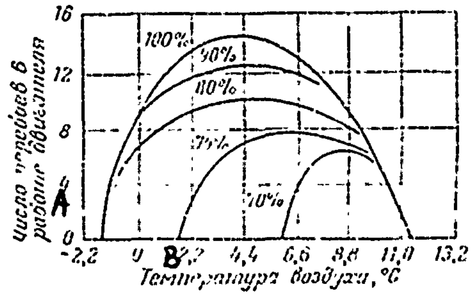

Fig. 94. Effect of air temperature and humidity on carburetor icing. The relative humidity is indicated next to the lines.

Key: A -- Number of missing events in engine operation
B -- Air temperature

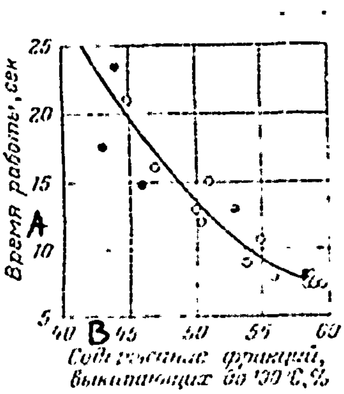

Fig. 95. Dependence of engine operating time before carburetor icing on the content in fuel of fractions boiling to 100° C.

Key: A -- Operating time, sec
B -- Content of fractions boiling to 100° C, percent

Table 65. Effect of additives on the number of engine stalls due to carburetor icing [15]

Топливо 1	Концентрация присадки, вес. % 2	Число остановок двигателя двух различных автомобилей 3	
Бензин без присадки 4	—	8,5	7,0
Бензин с присадкой 5			
изопропиловый спирт 6	0,5	1,3	0,7
То же 7	1,0	0	0
поверхностно-активная присадка МРА 8	0,005	2,5	1,7
То же 7	0,01	2,5	0,7

Key: 1 -- Fuel
2 -- Additive concentration, percent by weight
3 -- Number of stoppages in engines of two different motor vehicles
4 -- Nonadditive gasoline
5 -- Gasoline containing additives
6 -- isopropylalcohol
7 -- As above
8 -- MRA surfactant additive

The tendency of gasolines to cause carburetor icing is sometimes associated with the amount of light fractions in the gasoline boiling to 100° C. Fig. 95 presents the results of a determination of the engine operating time before stoppage due to carburetor icing as a function of the content of fractions boiling to 100° C, for 17 samples of commercial gasolines.

Heating a mixture or air in the engine intake manifold is an effective way of controlling carburetor icing. The mixture must be heated so that when fuel completely evaporates the mixture temperature does not drop below 3° C, that is, the temperature at which the condensing moisture can not yet freeze in the engine intake system or any humidity. Heating the intake manifold lowers the charge coefficient of the combustion chambers and reduces engine power, and therefore this means of controlling carburetor icing is used only in rare cases.

Recently special anti-icing gasoline additives have begun to be used in controlling carburetor icing. In tests made of 56 vehicles during the cold period of the year it was found that the additives reduce the number of engine operating interruptions due to carburetor icing from 511 cases down to 10. Various alcohols and their derivatives are used as anti-icing additives [45-54]; they are introduced in amounts from 0.5 to 2.0 percent. The butyl ester of diethylene glycol [51] is added, for example, in amounts up to 0.5 percent, and isopropyl alcohol — up to 2 percent [47, 48].

Surfactants preventing the "sticking" of ice to metal are very promising as anti-icing additives. These compounds proved to be effective in much lower concentrations than alcohols and their derivatives (Table 65).

It must be noted that the efficiency of anti-icing additives differs in different engines. The optimal concentration of additives in a gasoline must be selected with allowance for differences in engine design characteristics, and therefore foreign experience in using additives of this type can be applied to domestic automotive engines only after appropriate tests.

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[To Chapter Five]

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CHAPTER SIX

CHEMICAL STABILITY OF GASOLINES

Automotive gasolines, before use, must be transported and stored, sometimes for an extended time. During this period the most unstable compounds included in their composition undergo chemical changes on exposure to air oxygen, forming gummy compounds of complex composition (auto-oxidation). The ability of gasolines to withstand chemical changes in storage, transportation, and use is called chemical stability.

The chemical stability of commerical automotive gasolines depends on the composition and structure of their constituent hydrocarbons, on the content and nature of nonhydrocarbon impurities, and also on the effectiveness of the anti-oxidants added.

Oxidizability of various gasoline components

Method of evaluation. The oxidation of gasolines in conditions of storage or in the laboratory can be monitored by several indicators. Most often, indicators such as the oxygen content expended in oxidation, the content of acidic products (acidity), and the gum content (existent gum content) formed during oxidation, change in the color of the product in oxidation, content of peroxide compounds, etc., are determined.

The oxidation of gasoline initially proceeds very slowly and only after a certain interval of time does its rate rise. The time interval during which the oxidation is very low (absorption of oxygen is virtually not observed) is called the oxidation induction period. The longer its duration, the more stable the gasoline.

Determining the duration of the induction period during storage in atmospheric conditions is a overlengthy process, therefore, laboratory methods of determining the oxidation period in conditions of accelerated oxidation are employed. Oxidation is accelerated by raising the temperature from usually to 100° C. To avoid evaporation of the gasoline at a temperature this high, the oxidation is carried out under pressure in a special bomb.

According to the standard (GOST 4039-48) prevalent in the USSR, the duration of the induction period of automotive gasolines is determined in an oxygen bomb with an initial oxygen pressure of 7 atm in a boiling water bath. The time from the beginning of the experiment to the beginning of oxygen absorption is taken as the duration of the induction period.

Unfortunately, the induction period of gasoline determined in a laboratory in accelerated conditions does not always afford a precise enough prediction of the stability that this gasoline shows in storage. Changes have been noted when gasolines with a long induction period oxidized quite rapidly in storage, and conversely, gasolines with a short induction period were stored without change for a long time. We know, for example, that the stability of a gasoline containing an anti-oxidant is always greater in storage than a gasoline without this additive, even for the same oxidation induction period.

The difference between the rating of gasoline stability in laboratory conditions and in storage is probably accounted for by the different effect of the oxidation temperature conditions on the gasoline components. Increasing the oxidation temperature of a gasoline to 100° C evidently accelerates the oxidation of hydrocarbons of different structure, non-hydrocarbon impurities, and anti-oxidants by different amounts. Moreover, increased pressure is used when determining the duration of the induction period, which can also substantially affect the comparability of laboratory test data and actual storage data.

However, in spite of some drawbacks, the method of determining the duration of the oxidation induction period in an oxygen bomb found wide use in domestic and foreign practice in monitoring automotive gasoline quality.

Methods of rating the chemical stability of gasolines or their fractions at atmospheric or low excess pressure are employed in research practice. One of the first methods of this kind is described by Vorhees and Eisinger [1]. They oxidized gasoline at low pressure, with the amount of absorbed oxygen being measured using a mercury manometer. Later this method was improved by M. N. Mikhaylova and M. B. Neyman [2], S. S. Medvedev and A. N. Pod"yapol'skaya [3], K. I. Ivanov and Ye. D. Vilyanskaya[4].

B. V. Losikov, I. A. Rubinsteyn et al. [5] improved the method of measuring oxygen absorption. With their instrument, the product is oxidized at constant pressure, near-atmospheric, therefore the oxidation temperature must be lower than the initial-boiling point of the compound being oxidized.

The method of rating gasoline oxidizability in sealed ampules is of interest [6]. The simplicity of the equipment and the precision permit this method to be recommended for research purposes. Ampule-containing fuel is sealed in a snow bath at 0° C; the amount of oxygen absorbed during the oxidation time is measured in the same conditions barometrically.

In the methods described above for rating gasoline stability, temperature is the accelerating factor. However, in the literature there are accounts of methods of rating gasoline stability even at ordinary temperatures. These methods can be divided into two groups.

One group of methods provides for rating gasoline stability by exposure to various sources of light. However, these methods have not gained acceptance since the mechanism of photochemical oxidation evidently differs appreciably from ordinary oxidation occurring in gasoline storage. For example, it is assumed [2] that quanta of ultraviolet light, on being absorbed by the molecules of the compound, activate the process both at the surface and in the bulk, while in the absence of light oxidation proceeds predominantly from the surface.

The second group of methods provides for determining the chemical stability of gasolines by measuring their ability to react with several chemical compounds. This includes the method of sulfonic numbers developed by O. G. Pipik [7, 8].

The method involves estimating the reactivity of gasolines when they react with "activated" amylene fraction. The loss in the activity of this fraction depends on the tendency of the test gasoline to be oxidized. The gasoline stability is rated by the sulfonic number (sulfone is the product of the reaction of the amylene fraction with sulfur dioxide gas).

P. N. Kogerman [9] described a method of determining stability by measuring the heat of reaction of unsaturated hydrocarbons having two double bonds, with a solution of anhydrous tin chloride in dry benzene.

Chemical methods of rating gasoline stability have not gained acceptance because the tendency of hydrocarbons to oxidize in storage, and their tendency to react with given compounds do not always coincide. Tin chloride, for example, reacts with all dienic hydrocarbons, while primarily, dienic hydrocarbons with conjugated bonds participate in oxidation processes.

The above-described methods of accelerated gasoline oxidation at elevated temperatures, besides the measurement of oxygen absorption, often provide for the analysis of the oxidized gasoline with a determination made of the oxidation products, including the gum content.

It has long been noted that the higher the gum content in gasoline, the more deposits are formed in the engine intake system. On this basis, methods were developed for determining the gum compounds in gasolines that can deposit in the intake system. The conditions of the methods reproduce to the fullest the conditions in which gasoline evaporates in the intake system. Gasoline in a small beaker or a cup is evaporated at an elevated temperature with heated air (GOST 1567-56) or by water vapor (GOST 8489-58) in a special instrument. Gum compounds remaining in the beaker or the cup after gasoline evaporation are customarily called the "existent" gums, that is, gums which at a given moment are actually present in a gasoline. This name is not altogether exact, since during the sweeping of gasoline with air at elevated temperatures oxidation of a gasoline occurs and new gums are formed, which then are determined as "existent". However, the term is so widespread that it is hardly worthwhile introducing a new one.

In contrast to methods of determining existent gums in gasoline, there are methods for determining so-called "potential" gums. These methods are used to determine the gum content in a gasoline after the gasoline has been oxidized to a certain extent. In other words, these methods characterize the potentiality of gasolines to form gum compounds upon oxidation. One of the most common methods of determining potential gums in gasoline is the "copper cup" method, which gained wide acceptance in foreign practice of monitoring automotive gasoline quality. The method involves oxidizing and evaporating a gasoline sample in a copper cup at elevated temperatures. The copper catalytically accelerates gasoline oxidation, and in a short time it is possible to rate the tendency of the gasoline to form gum compounds during oxidation.

It must be noted that the content of gum compounds which is determined as existent or potential gums represents only a small fraction (from 10 to 35 percent) of the oxygen compounds present in gasoline. Only high-molecular gum compounds formed due to the condensation of the primary oxidation products remain in the beakers or cups. All oxygen compounds whose molecular weights differ only slightly from the molecular weight of the gasoline hydrocarbons are evaporated together with the hydrocarbon portion of the gasolines.

To estimate the total content of oxygen compounds in a gasoline, adsorption methods of analysis are most suitable. Oxygen compounds of gasolines together with other nonhydrocarbon impurities adsorb readily on silica gel or activated aluminum oxide. The content of these "adsorption" gums in gasoline is always several times higher than the existent gum content.

Auto-oxidation of hydrocarbons. The basis of modern concepts concerning the mechanism of liquid-phase oxidation, in particular, the auto-oxidation of hydrocarbons, is the Bach-Engler peroxide theory [10-12], and the N. N. Semenov theory of branched chain reactions [12, 13, 14 Fundamental work by V. N. Kondrat'yev, S. S. Medvedev, K. I. Ivanov, N. M. Emanuel', M. B. Neyman, N. I. Chernozhukov, S. E. Kreyn, and other Soviet scientists played an enormous role in formulating oxidation theory [15-17].

According to modern concepts, the oxidation of hydrocarbons is a complex multistage process developing via peroxides and free radicals. In general form, the mechanism of hydrocarbon oxidation can be represented by a scheme that includes the following elementary stages:

initiation of a chain

$$RH \xrightarrow{O_2} R\cdot$$

chain development

$$R\cdot + O_2 \rightarrow ROO\cdot$$

$$RO\dot{O} + R_1H \rightarrow ROOH + \dot{R}_1$$

degenerate branching of chain

$$ROOH \rightarrow R\dot{O} + \dot{O}H$$

molecular decomposition

$$ROOH \rightarrow \text{Stable products}$$

chain rupture

$$\dot{R} + \dot{R}_1 \rightarrow R - R_1$$

The hydroperoxides accumulating in this system undergo degradation at the O-O bond, which has a relatively low energy of activation (30-40 kcal/mole) [16], forming not only active radicals prolonging the oxidation chain, but also relatively stable oxidation products (alcohols, compounds containing a carbonyl group, etc.).

This radical-chain scheme most fully accounts for features of the auto-oxidation of hydrocarbons (the presence of an induction period, its auto-catalytic nature, and high sensitivity to traces of foreign impurities) and satisfactorily agrees with extensive experimental data. Most data published in the literature relate to the oxidation of individual hydrocarbons. But the oxidation of polycomponent systems as complex as gasolines has been little studied.

It was established that hydroperoxides are the primary oxidation products of hydrocarbons [15]. Hydroperoxides retain the structure of the hydrocarbon radical. When certain unsaturated hydrocarbons are oxidized, according to modern concepts, the primary oxidation products can also be diatomic hydroperoxides, in addition to monoatomic hydroperoxides [18]. The probability of oxygen addition at the C-H bond, with the formation of hydroperoxides, increases in the following series: primary $<$ secondary $<$ tertiary carbon atom.

Alkane and cyclane hydrocarbons are oxidized at lower rates when at low temperatures [15, 16]. The introduction of oxygen at primary C-H bonds at low temperatures virtually occurs not at all. The tendency of hydrocarbons to oxidation rises with increase in molecular weight.

The oxidizability of aromatic hydrocarbons depends significantly on their structure. Aromatic hydrocarbons containing no side chains, especially monocyclic, are highly resistant to oxygen and in the conditions we are considering do not oxidize at all. Alkylaromatic hydrocarbons, just as polycyclic in which the rings are connected with an aliphatic bridge, are oxidized relatively facilely at low temperatures. Oxygen is added on most readily at the C-H bond in the alpha-position to the aromatic ring. Here the difference in the oxidizability of the primary, secondary, and tertiary C-H bond of the side chain, even though persisting, is still less distinctly manifested [19].

The presence of a quaternary carbon atom in the alpha-position to an aromatic ring sharply enhances the resistance of alkylaromatic hydrocarbons to oxidation. Oxidizability increases with increase in the length and number of side chains in a molecule.

The greatest oxidizability in low temperatures is found for unsaturated hydrocarbons and, above all, diolefinic hydrocarbons, of either cyclic or aliphatic structure with conjugated double bonds [20]. Dialiphatic hydrocarbons with double bonds distant from their center are similar to monoolefinic hydrocarbons in their oxidizability. The oxidizability of monoolefinic hydrocarbons is significantly increased as the double bond is advanced toward the center of the molecule and as the branching is increased. Of the monoolefinic hydrocarbons, aromatic hydrocarbons with an unsaturated side chain are oxidized especially readily [21, 22].

Based on experimental data, unsaturated hydrocarbons with the same molecular weight can be linked as follows in oxidizability at low temperatures: cyclic diolefins with conjugated double bonds > aliphatic diolefins with conjugated double bonds > aromatic mono-olefins > cyclic olefins with a single double bond with the ring > diolefins with widely separated double bonds > aliphatic mono-olefins.

A study of the structure of primary peroxides obtained by oxidizing a number of individual hydrocarbons of different structural types by K. I. Ivanov [15] showed that the oxidation of unsaturated hydrocarbons at low temperatures occurs not at the double bond, but at the C-H bond adjoining carbon atoms connected with a double bond. For example, in the oxidation of hexene, hexene peroxide is obtained, and in the oxidation of cyclohexene -- -- cyclohexene peroxide.

The primary products of hydrocarbon oxidation -- hydroperoxides -- are capable of undergoing various transformations [15, 16, 23-39]:

decomposition with the formation of alcohols and ketones;

condensation with carbonyl compounds, forming oxyalkyl peroxides;

oxidative decomposition, forming polyatomic peroxides, with the subsequent oxidation of the decomposition products into acids and oxy-acids;

intramolecular rearrangement, with the formation of peroxides having a different structure;

polymerization with the peroxide group retained; and

oxidation of the initial compound by hydroperoxides.

Depending on the hydroperoxide structure and the conditions of the process, any one of the above-listed directions can dominate.

In the oxidation of mixtures of hydrocarbons, the primary oxidation products of various hydrocarbon classes react with each other, which is responsible for the diversity of the resulting products. Here the oxidation products of one hydrocarbon class can affect the rate and direction of oxidation of hydrocarbons in other classes.

N. I. Chernozhukov and S. E. Kreyn [40], based on extensive experimental material on the oxidizability of artificial mixtures of hydrocarbons, concluded that aromatic hydrocarbons, when in a mixture with naphthenic hydrocarbons, protect the latter against oxidation, and the extent of their influence depends on structure and concentration in the mixture. The authors attribute the inhibiting action of aromatic hydrocarbons to the anti-oxidant properties of their oxidation products.

Unsaturated hydrocarbons have an especially strong effect on the oxidation of hydrocarbon mixtures. When they are present, even hydrocarbons which would not be oxidized by themselves in these conditions sometimes are subjected to oxidation. It must be noted that even a small (less than 1 percent) content of reactive unsaturated hydrocarbons, such dienic and alkylaromatic hydrocarbons with a double bond in the side chain, renders virtually any hydrocarbon mixture capable of oxidation by air oxygen at ordinary temperatures.

Whereas a certain amount of experimental material on primary oxidation products and their decomposition directions is available and the general correlations have been formulated, the processes of the further transformation of oxidation products into gums have been completely uninvestigated. Data on the elementary composition, effect of iodine number, and the presence of functional groups indicates that gum compounds result from oxidative polymerization and oxidative condensation of the decomposition products of hydroperoxides with the participation of nonhydrocarbon impurities. Among nonhydrocarbon components in gasolines, oxygen and sulfur compounds are most significant in oxidation processes.

Effect of phenol type compounds. Oxidation compounds contained in gasoline affect its stability to some extent. For the most part they promote more rapid oxidation and thus lower the chemical stability of the fuel. However, oxygen compounds of the phenol type have anti-oxidant properties and the chemical stability of gasolines is enhanced when they are present. N. V. Razumov [41] showed that oxygen compounds with anti-oxidant properties can enter gasoline from crude, primarily in the destructive refining of the crude. He established that these "natural" anti-oxidants are phenol type compounds.

A sample of gasoline refined by the thermal cracking of mazut from Ekhabi crude contained about 0.25 percent phenols, while straight-run gasoline refined from the same crude had no phenols. Thermal cracking gasoline refined from mazut obtained from this same crude had a phenolic content so appreciable that no special anti-oxidants had to be added. The oxidation induction period for this gasoline was 600-900 minutes.

Recently, the content of phenolic compounds in commercial automotive gasolines and their components [42] was determined with a specially developed colorimetric method [43]. It was shown [43] that the content of phenol type compounds in gasolines fluctuates within appreciable limits. Natural anti-oxidants are present to a lesser extent in catalytic-process gasolines than in thermal cracking gasolines. Sulfuric acid scrubbing of thermal cracking gasolines sharply reduces the content of phenolic compounds. Phenolic compounds are absent in straight-run gasolines.

The effectiveness of natural anti-oxidants of the phenolic type was investigated [44] with three samples of thermal cracking gasolines prepared in roughly the same process regimes from mazuts obtained from Nebitdag crude, and a blend of Baku crudes and Tuymazi crude (Table 66).

The gasolines tested contained virtually the same content of unsaturated hydrocarbons (based on iodine number), but differed appreciably in their content of natural inhibitors. These results show that the effectiveness of phenolic compounds contained in gasolines is extremely low. The oxidation induction period of gasolines refined from Tuymazy and Baku crudes is only 145-190 minutes when the phenolic contents are present at an appreciable level. The high effectiveness of phenolic compounds in gasolines refined by the thermal cracking of Ekhabi mazut is evidently due to the structure of the oxygen compounds in Ekhabi crude.

Effect of organic sulfur compounds. A study of the effect of sulfur compounds on the oxidation of gasolines containing unsaturated hydrocarbons is of particular interest, since the oxidizability of some organic sulfur compounds is very close to the oxidizability of unsaturated hydrocarbons. The latter fact suggests that the effect of organic sulfur compounds on the oxidizability of saturated and unsaturated hydrocarbons can differ widely.

The effect of organic sulfur compounds on the oxidizability of fuels containing unsaturated hydrocarbons depends to a large extent on the presence and nature of anti-oxidants [45, 46]. Mercaptans, sulfides, and disulfides inhibit the oxidation of gasolines not containing anti-oxidants. When gasolines containing mercaptans undergo oxidation, in the first hours the amount of absorbed oxygen rises somewhat, but then decreases; the oxygen absorption

Table 66. Chemical composition and stability of gasolines refined by the thermal cracking of various crudes

1 Бензин, полученный в результате крекинга	2 Содержание непредельных углеводородов, вес. %	3 Малеиновое число *, г I_2/100 г	4 Содержание природных ингибиторов, % триоксибензола	5 Содержание серы, %	6 Индукционный период, мин
Небитдагской нефти 7	43	7,5	0,009	0,01	60
Смеси бакинских нефтей 8	46	4,3	0,063	0,01	190
Туймазинской нефти 9	48	4,7	0,107	0,13	145

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* The maleic number characterizes the content of dienic hydrocarbons.

Key:
1 -- Gasoline prepared by cracking
2 -- Content of unsaturated hydrocarbons, percent by weight
3 -- Maleic number*, g of I_2/100 g
4 -- Content of natural inhibitors, percent of trioxybenzene
5 -- Sulfur content
6 -- Induction period, minutes
7 -- Nebitdag crude
8 -- Blends of Baku crude
9 -- Tuymazi crude

curves show an inflection. At the first stages of oxidation, some of the absorbed oxygen evidently is used up in initiating the oxidation of the mercaptans as such.

The greatest inhibiting effect results from adding aromatic mercaptans to gasoline. Mercaptans containing aliphatic and naphthenic hydrocarbon radicals exhibit a lower inhibiting action. It is also important that the inhibiting ability of mercaptans depends on their structure. Octylmercaptan of normal structure has a higher anti-oxidizing action than secondary and tertiary octylmercaptans. The inhibition of the oxidation of gasoline in the presence of mercaptans is accompanied not only by a reduction of the amount of absorbed oxygen, but also by a reduction in the existent gum content and in the acidity (Table 67).

The oxidation of organic sulfur compounds in gasolines is accompanied by a change in their color (cf. Table 67). These data indicate that the inhibiting action of organic sulfur compounds is accompanied by their oxidation, and this results in the increased optical density of gasolines containing these compounds [47, 48].

Until recently, it was believed that more intensely colored gasolines contain a higher existent gum content. However, sometimes light gasolines can contain a higher gum content than dark gasolines. The data in Table 67 enable us to establish several reasons for this phenomenon. All gasolines contained the same amount of S — 0.05 percent, however they differed widely in color after oxidation. Gasolines containing sulfur compounds revealing the greatest inhibiting effect proved to be the most intensely colored. The existent gum content was the lowest in the darkest gasolines. Gasoline containing 0.05 percent S in the form of benzylmercaptan darkened quite rapidly at the outset of oxidation and subsequently its color remained roughly constant. With increase in the mercaptan sulfur content, the color of the gasoline becomes darker after oxidation.

Since the increase in the optical density of gasolines is associated with the oxidation of organic sulfur compounds and, especially, mercaptans, during oxidation the mercaptan sulfur content in gasoline must diminish. A test of this correlation confirmed (Fig. 96) the relationship prevailing between the rise in the optical density of gasoline and its consumption of mercaptan sulfur. Aromatic mercaptan, in contrast to aliphatic, has higher inhibiting properties, is consumed more rapidly and more intensively, and colors gasoline.

Thus, these results suggest that the variation in the color of gasoline observed during its storage time is mainly due to the amount and composition of its content of organic sulfur compounds. When hydrocarbon mixtures containing anti-oxidants undergo oxidation, the effect of organic sulfur compounds is somewhat different.

Adding organic sulfur compounds to gasolines containing anti-oxidants has virtually no effect on the oxidation induction period. It can be assumed that during the induction period, that is, during the time when the anit-oxidant counteracts the oxidation of hydrocarbons, the role of sulfur compounds is limited. The sulfur compounds as such during this period, in the absence of initiating action of the primary products, do not undergo oxidation [49-59].

During the induction period no interaction between anti-oxidant and organic sulfur compounds evidently occurs. The ability of an anti-oxidant such as di-sec-butyl-p-phenylene diamine to accelerate the oxidation of mercaptans [49], observed in the literature, relates primarily to the characteristics of precisely this anti-oxidant and, secondly, is involved with its catalytic effect and is not accompanied by the consumption of the anti-oxidant and the reduction in the chemical stability of gasolines.

Table 67. Characteristics of the oxidation products (at 110° C, for 5 hours) of the 130-170° C fraction of A-72 gasoline with different sulfur compounds present (0.05 percent S)

Продукт 1	Поглощение кислорода за время окисления, мл O_2/20 г 2	Содержание фактических смол, мг/100 мл 3	Кислотность, мг KOH/100 мл 4	Оптическая плотность 5
Исходный бензин 6	133	554	79,4	0,09
Тот же бензин 7				
с бензилмеркаптаном 8	28	195	19,2	1,03
с α-фенилэтилмеркаптаном 9	30	225	19,7	0,75
с н-октилмеркаптаном 10	42	256	30,4	0,80
с *втор*-октилмеркаптаном 11	53	330	31,3	0,72
с циклогексилмеркаптаном 12	55	341	35,0	0,63
с *трет*-октилмеркаптаном 13	68	356	46,7	0,46
с дибутилсульфидом 14	82	382	63,2	0,16
с диизоамилсульфидом 15	112	415	85,5	0,13

Key:
1 -- Product
2 -- Absorption of oxygen during the oxidation period, ml of O_2/20 g
3 -- Existent gum content, mg/100 ml
4 -- Acidity, mg of KOH/100 ml
5 -- Optical density
6 -- Initial gasoline
7 -- Initial gasoline
8 -- containing benzylmercaptan
9 -- containing alpha-phenylethylmercaptan
10 -- containing n-octylmercaptan
11 -- containing sec-octylmercaptan
12 -- containing cyclohexylmercaptan
13 -- containing ter-octylmercaptan
14 -- containing dibutylsulfide
15 -- containing diisoamylsulfide

Oxidizability of commercial gasolines. The tendency of commerical automotive gasolines and their components to undergo oxidation depends both on the composition and the structure of hydrocarbons, as well as the content and nature of the nonhydrocarbon impurities. The chemical composition of gasolines is determined by the quality of the crude and the gasoline refining technology.

Thermal cracking and reforming gasolines contain a significant content of reactive unsaturated hydrocarbons and have low chemical stability:

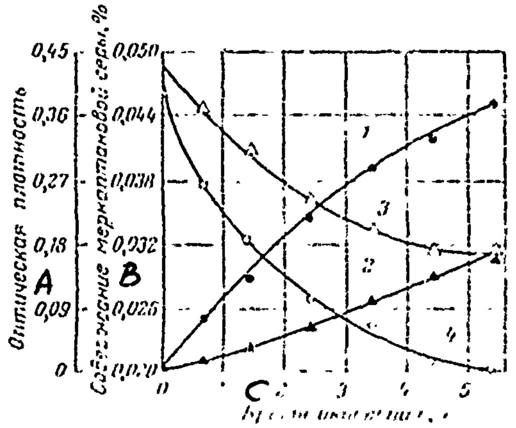

Fig. 96. Optical density of gasolines and their mercaptan sulfur content as functions of the oxidation time (the experiments were conducted on the 130-170° C fraction of catalytic cracking gasoline containing 0.05 percent S, at 110° C):

1 -- Optical density of gasoline containing benzylmercaptan
2 -- Optical density of gasoline containing hexomercaptan
3 -- Content of mercaptan sulfur in gasoline containing benzylmercaptan
4 -- Content of mercaptan sulfur in gasoline containing hexylmercaptan
Key: A -- Optical density
B -- Content of mercaptan sulfur
C -- Oxidation time, hours

	Induction period, minutes
Thermal cracking gasoline	
from Tuymazy crude	205
blend of Tatar and Tuymazy crudes	185
blend of Baku crudes	190
blend of Groznyy crudes	225
Bavly crude	145
Shugurovo crude	190
Thermal reforming gasoline	
from Tuymazy crude	120
blend of Tatar and Tuymazy crudes	100
blend of Tatar crudes, sample 1	120
as above, sample 2	90
blend of Bashkir crudes	120

The duration of the oxidation induction period of thermal cracking gasolines usually does not exceed 200-250 minutes, while for thermal reforming gasolines it is not longer than 100-120 minutes.

More stable gasolines are produced by catalytic methods of refining crude. But here also one must bear in mind that the automotive gasoline component obtained by catalytic cracking can be an unstable product. In our country, for a long time catalytic cracking gasoline was used only in compounding aviation gasolines. The component of aviation gasolines was produced using the scheme of two-stage catalytic cracking and its stability was wholly satisfactory.

Catalytic cracking gasoline used as an automotive gasoline component is produced by cracking crude in a single stage without scrubbing of the distillate. This measure increases the facility of the unit and lowers the cost of the gasoline, but a considerable content of unsaturated hydrocarbons (20-30 percent) remains in the catalytic cracking gasoline and its stability is lowered (60]. Moreover, a heavier crude can be used in catalytic cracking in producing the automotive component, which is also accompanied by a loss in the chemical stability of gasolines.

Below are presented comparative data of laboratory tests made of thermal cracking gasoline and single-phase catalytic cracking gasoline, obtained by refining Tuymazy crude:

	Thermal cracking gasoline	Catalytic cracking gasoline
Existent gum content, mg/100 ml:		
initial value	8	6
after oxidation with copper strip at 100° C during the time indicated		
2 hours	58	17
4 hours	83	23
Induction period, minutes		
without metal present	180	855
in the presence of copper	55	430

Gasoline prepared by catalytic cracking, even in the single-stage process, has higher stability than thermal cracking gasoline. These data were confirmed also in the actual storage of these gasolines (Fig. 97).

However, it must be considered that the component of catalytic cracking gasoline is used in compounding high-octane gasolines intended for use in high-rpm engines with high charge factor. These engines impose intensified requirements on gasoline quality. In particular, the existent gum content must not exceed 10 mg/100 ml, while gasolines containing a gum content up to 20 mg/100 ml are allowed to be used in older-model engines.

Gasolines prepared by single-stage catalytic cracking as a rule contain a significant content of natural anti-oxidants of the phenol type and have a long oxidation induction period. But natural anti-oxidants are marked by low effectiveness in actual storage conditions and gum formation, when they are present, proceeds quite intensively. So the relationship between the induction period and the actual storage time for catalytic cracking gasolines is not the same as for other gasolines [61].

Catalytic reforming gasolines are nearly entirely free of unsaturated hydrocarbons and are marked by high chemical stability. However, the high content of aromatic hydrocarbons makes catalytic reforming gasolines less stable than straight-run gasolines (Fig. 98). The acidity increases during oxidation in catalytic reforming gasoline to a greater extent than does the existent gum content. This correlation was confirmed not only by laboratory data, but also from results of the experimental storage of these gasolines in vehicle fuel tanks (Table 68).

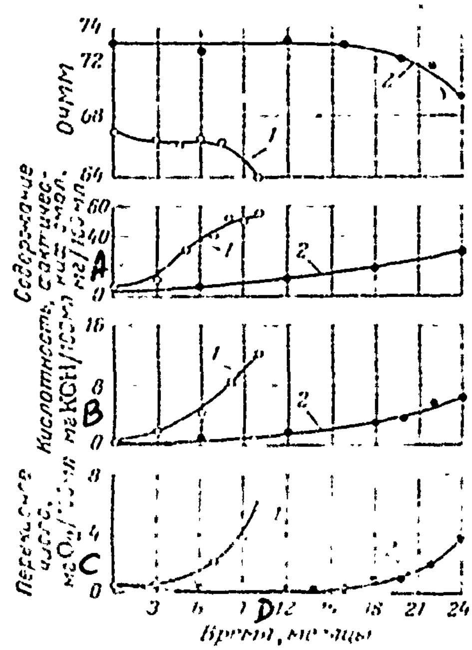

Fig. 97. Change in properties of automotive gasolines during storage:
1 — Thermal cracking gasoline
2 — Catalytic cracking gasoline
Key: A — Existent gum content, mg/100 ml
B — Acidity, mg of KOH/100 ml
C — Peroxide number, mg of O_2/100 ml
D — Time, months
E — ONMM

Thus, the most stable component of commercial automotive gasolines is straight-run gasoline, somewhat lower is the stability of catalytic reforming gasoline, even less stable are catalytic cracking and thermal cracking gasolines, and least stable is thermal reforming gasoline. Other automotive gasoline components, for example, the products of alkylation, polymerization, isomerization, hydrogenation, and the like have high chemical stabilities.

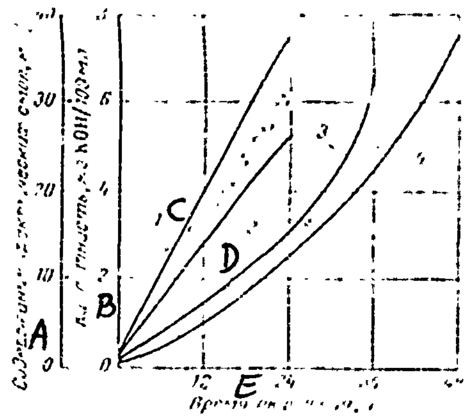

Fig. 98. Oxidizability of straight-run and catalytic reforming gasolines (110° C, copper):
1,4 — Acid number
2,3 — Existent gum content
Key: A — Existent gum content, mg/100 ml
B — Acidity, mg of KOH/100 ml
C — Reforming gasoline
D — Straight-run gasoline
E — Oxidation time, hours

To ensure the stability of commercial automotive gasolines, existing specifications (GOST 2084-67) provide for the addition to catalytic cracking and thermal-process gasolines of special anti-oxidants.

Anti-oxidant additives

Adding anti-oxidants is the most effective and economically advantageous, and sometimes even the only possible way of enhancing the chemical stability of automotive gasolines. This method of stabilizing gasolines has been used on a commercial scale for several decades.

Modern views as to the mechanism of anti-oxidant action in gasolines are based on the peroxide theory of oxidation involving a chain mechanism. The oxidation of hydrocarbons are classified as chain degenerate-branched reactions. The scheme that is generally accepted and best-supported at the present time assumes that the free hydrocarbon radical R• formed in the initial oxidation stage reacts with oxygen, forming the peroxide radical ROO•, which on reacting with a new hydrocarbon molecule yields hydroperoxide and a new radical. The breakdown of the hydroperoxide leads to chain branching, therefore the reaction is autocatalytic. Rupture of the chains in a medium containing no anti-oxidants occurs mainly due to the recombination of the radicals.

Table 68. Change in the quality of catalytic reforming and straight-run gasolines in vehicle fuel tanks

Бензин 1	2 Содержание фактических смол, мг/100 мл		5 Кислотность, мг KOH/100 мл	
	3 в начале хранения	4 через 2 года	3 в начале хранения	4 через 2 года
Новые баки 6				
Прямой перегонки 7	3	3	0,2	0,4
Каталитического риформинга 8	3	4	0,1	0,7
Баки, бывшие в эксплуатации 9				
Прямой перегонки 10	3	5	0,2	2,3
Каталитического риформинга 11	4	7	0,4	3,1

Key:
1 — Gasoline
2 — Existent gum content, mg/100 ml
3 — at the outset of storage
4 — in 2 years
5 — Acidity, mg KOH/100 ml
6 — New tanks
7 — Straight-run
8 — Catalytic reforming
9 — Tanks previously in service
10 — Straight-run
11 — Catalytic reforming

Reaction of anti-oxidants reduces to rupture of the chain resulting from the reaction of one of the radicals participating in the chain with the anti-oxidant molecules HA or X. This reaction may be either the exchange reaction

$$ROO\cdot + HA \rightarrow ROOH + A\cdot$$

or the addition reaction

$$ROO\cdot + X \rightarrow ROOX\cdot$$

In either of these two cases, a low-active radical is capable of extending the chain forms as a result of the reaction. The anti-oxidant radicals can recombine again into a molecule with anti-oxidant properties.

The anti-oxidant molecule can be decomposed not only by radicals of the type R• and ROO•, but also by radicals formed in the decomposition of hydroperoxides — RO• and •OH. In particular, one of the anti-oxidant classifications [53] divides them into "inhibitors of free radicals" and "peroxide decomposing agents."

Since the reaction of liquid-phase oxidation of hydrocarbons is autocatalytic, the concentration of free radicals during the reaction rises sharply. The anti-oxidant inhibits the buildup of oxidizing reactions for sometime (the induction period), after which the oxidation rate rises sharply. Acceleration of the oxidation process during the induction period can be caused by the following factors:

the anti-oxidant molecules evidently cannot react with all the free radicals, therefore with time the radicals not reacting with the anti-oxidants can accumulate;

some of the anti-oxidant is expended in side reactions unrelated to rupture of the oxidizing chains, and as a result the anti-oxidant concentration decreases; and

not all anti-oxidant radicals formed in the reaction of an anti-oxidant with hydrocarbon radicals are regenerated, which also leads to a lower anti-oxidant concentration.

Thus, the accumulation of free radicals of unusual structure and the reduction of anti-oxidant concentration lead to the termination of the induction period and the acceleration of the oxidation of hydrocarbon fuels.

Compounds containing an amine group or an oxi-group have gained the widest acceptance as anti-oxidants for hydrocarbon fuels. The effectiveness of these additives is determined by the lability of the hydrogen atom in these groups [62]. Compounds that are difficult to oxidize as a rule virtually break no reaction chains and are poor anti-oxidants. Readily oxidizable compounds are rapidly used up in side reactions and direct oxidation by air oxygen, and as a result have no inhibiting action on the primary process.

Egloff et al. [63] showed that only those compounds that exhibit moderate oxidation-reduction potentials (from 0.609 to 0.797 v) are effective anti-oxidants. Fieser [64] determined that the optimal oxidation-reduction potential of good inhibitors is in the range 0.700-0.800 v. However, the values indicated by Egloff and Fieser are in need of verification, since the procedures in these experiments had essential defects [65].

The concepts presented above concerned with the action of anti-oxidants indicate that adding anti-oxidants does not eliminate the oxidation of hydrocarbon fuels, but inhibits it, by prolonging the induction period. From this point of view, anti-oxidants for gasolines can be subdivided [66] into products predominantly inhibiting specifically oxidizing reactions (occurring with the significant consumption of oxygen) — "anti-oxidants", and products primarily inhibiting secondary processes (polymerization and condensation) leading to gum formation — "gum formation inhibitors." The first of the fuel oxidation inhibitors includes primarily amines and some aminophenols, and the second -- phenols. Aminophenols and screened alkylphenols as a rule manifest either function.

The anti-oxidant properties of phenols depend on their structure. Studies by M. D. Tilicheyev, M. B. Vol'f, and O. V. Vasil'yeva (Pletneva), N. M. Silishchenskaya, I. P. Uvarov et al. [67-71] established that the main components responsible for the maximum effectiveness of phenol type anti-oxidants are polyatomic phenols and some of their dimethyl*, in particular, the dimethyl ester of pyrogallol. It was shown that anti-oxidant properties are mainly exhibited by phenols with hydroxyl groups located side by side (o-dihydroxybenzenes, pyrocatechin, pyrogallol, and homologs). Products rich in phenolic compounds of various structures are obtained in the thermal refining of solid fossil fuels.

Shale refining products. Phenols used as crosstie-impregnating material, setting material for plastics, bakelite, varnishes, etc. are extracted from the semicoking tar obtained from Baltic shale on an industrial scale. To extract the phenols, the tar or its fractions are treated with an aqueous solution of alkali. The solution of phenolates thus obtained is scrubbed with benzene or with light gasoline to free them of neutral oils and then the solution is decomposed with mineral acid to isolate the free phenols.

Tar obtained from shales, according to the data of Kh. T. Raudsepp [72], contains about 30 percent phenols, whose composition includes -- in addition to phenol homologs -- indanoles, naphthols, diatomic phenols, and phenols containing an ester group (higher alkyl esters of diatomic phenols and heterocyclic phenols of the hydroxycoumarone type). Unfortunately, the content of diatomic phenols in shale resins is low.

Phenols extracted from the middle (180-350° C) fraction of generator tar of Baltic shales have the following group composition (in percent):

Hydroxy derivatives of benzene	
phenol and cresols	10
xylenols	24
alkylphenols, containing C_3-C_6 radicals in side chains	24
Hydroxy derivatives of naphthalene	18
Dihydroxy derivatives of benzene	8
Dihydroxy derivatives of naphthalene	10

Phenols extracted from the central fraction of tunnel tar are of approximately the same composition. Phenols from fractions boiling above 300° C are more complex compounds, mainly derivatives of naphthols.

Table 69. Relative effectiveness of phenols prepared from shale tars as anti-oxidants (added to gasoline in the amount 0.065 percent by weight)

Антиокислитель 1	По индукционному периоду 2	По поглощению кислорода 3	По смолообразованию 4
Бензин с древесносмольным антиокислителем (ГОСТ 3181-67) 5	1,00	1,00	1,00
То же, с фракциями сланцевых фенолов, °C 6			
180—200	0,81	0,[illegible]	0,7[illegible]
200—300	0,76	0,8[illegible]	[illegible]
300—380	1,01	1,31	[illegible]
308—330	1,12	1,50	[illegible]

Key: 1 — Anti-oxidant
2 — Based on induction period
3 — Based on absorption of oxygen
4 — Based on gum formation
5 — Gasoline containing lignoresin anti-oxidant (GOST 3181-67)
6 — As above, containing the shale phenol fractions indicated below, ° C.

The effectiveness of shale phenols was tested with several gasolines by determining the induction period according to GOST 4039-48 and the oxidation time to the absorption of 10 ml of oxygen and the formation of gums in the amount of 25 mg/100 ml.

Shale phenols exhibit adequate solubility in fuels and can be added to gasolines without using intermediate solvents. Some of the most typical test results are shown in Table 69.

From the data in Table 69 we see that shale phenols exhibit the properties of anti-oxidants; their effectiveness rises with the boiling point limits of the tar fractions from which they were isolated. In length of of induction period and inhibition of oxygen absorption, the lighter shale phenols are inferior, while the heavier surpass the commercial lignoresin anti-oxidant. However, in effectiveness of inhibiting gum formation, shale phenols are significantly inferior to the lignoresin anti-oxidant. Thus, phenols isolated from shale tars have low anti-oxidant properties and their use as anti-oxidants to automotive gasolines can prove advisable only in limited amounts at refineries located near shale combines.

Coal refining products. Effective anti-oxidants containing more than 50 percent diatomic phenols were found in the products of the semicoking of coals. Various samples of crude phenols from semicoking tars and tar water were investigated as anti-oxidants, along with narrow fractions of the phenols prepared by distilling crude phenols under vacuum (Table 70).

Table 70. Relative effectiveness of phenols prepared from coal semicoking tar as anti-oxidants (added to gasoline in the amount 0.065 percent by weight)

Антиокислитель 1	По индукционному периоду 2	По смолообразованию 3
Древесносмольный антиокислитель (ГОСТ 3181—67) 4	1,00	1,00
Фенолы из смолы полукоксования (фракция 240—330 С) 5	1,34	4,30
Узкая фракция фенолов из смолы полукоксования (фракция 230—270° С) 6	2,59	4,80
Фенолы из керосиновой фракции смолы полукоксования, образец 1 7	1,05	1,00
То же, образец 2 8	1,13	1,20
Фенолы из бензино-лигроиновой фракции смолы полукоксования 9	0,91	0,73
Фракции двухатомных фенолов, выделенных из подсмольной воды 10	2,47	8,00

Key: 1 — Anti-oxidants
2 — Based on induction period
3 — Based on gum formation
4 — Lignoresin anti-oxidant (GOST 3181-67)
5 — Phenols from semicoking tar (240-330° C fraction)
6 — Narrow fraction of phenols from semicoking tar (230-270° C fraction)
7 — Phenols from the kerosene fraction of semicoking tar, sample 1
8 — As above, sample 2
9 — Phenols from the gasoline-ligroin fraction of semicoking tars
10 — Fractions of diatomic phenols isolated from tar water

Phenols extracted from semicoking tars prepared from Cheremkhovo coals can serve as anti-oxidants for automotive gasolines. A phenol sample distilled in the range 240-330° C proved to have the highest effectiveness, among the fractions tested.

From these data it follows that phenols of coal origin include effective anti-oxidants significantly exceeding the lignoresin anti-oxidant. Thus, some fractions of diatomic phenols isolated either from semicoking tars or from tar water prove to be more than twice as effective as the lignoresin anti-oxidant when rated by induction period, and nearly five times more effective when rated by the inhibition of gum formation in gasoline (cf. Table 70). Composite phenols prepared from tar water and the 240-330° C phenol fraction prepared from the semicoking tar of Cheremkhovo coals showed anti-oxidizing properties. Phenols isolated from the kerosene fraction of semicoking tar are virtually equivalent in effectiveness to the lignoresin anti-oxidant, while phenols isolated from the gasoline-ligroin fraction are less effective than the lignoresin anti-oxidant. It must be noted that phenols prepared from the products of coal semicoking are especially effective in inhibiting gum formation when gasolines are oxidized in the presence of metals (cf. Table 70).

Crude phenols isolated from tar water using butylacetate are a mixture of mono- and diatomic phenols with an admixture of solid particles and high-boiling tarry substances. The composition of crude phenols prepared from tar water include [73] about 50 percent monoatomic phenols (18 percent phenol, 24 percent cresol, 5 percent xylenols, and about 3 percent high-boiling monoatomic phenols), 23 percent pyrocatechin and its homologs, and 14 percent resorcinol and its homologs. The solid residue after distilling the crude phenols is as much as 10 percent.

A narrow fraction of diatomic phenols isolated from crude phenols present in tar water and revealing high effectiveness in stabilizing gasolines contained more than 50 percent pyrocatechin and its homologs, more than 30 percent resorcinol and its homologs and 12-20 percent monoatomic phenols.

The effectiveness of phenols isolated from tar water was found to be high in all the gasoline samples investigated. (Table 71).

Phenols from tar water were found to be approximately twice as effective as the lignoresin anti-oxidant; they satisfactorily stabilized both gasoline without any antiknock, as well as gasolines containing tetraethyl lead. Special experiments showed that adding coal-origin phenols to automotive gasoline increases its chemical stability and does not deteriorate other physicochemical properties.

When a study was made of phenols from tar water, special attention was given to the ability of these phenols to be washed out of gasolines with water [74]. These phenols can be extracted with water from gasolines to a greater extent than phenols from semicoking tar or phenols of the lignoresin anti-oxidant (Table 72). However, gasoline containing phenols from tar water, and also after treatment with water in very drastic conditions retains a high level of stability.

A check of prolonged storage showed that phenols from tar water are effective anti-oxidants and their use significantly extends the allowable storage time for automotive gasolines. At the present time the FCh-16 anti-oxidant is used for the chemical stabilization of automotive gasolines at many oil refineries in our country.

Refined wood products. One of the first commercial anti-oxidants finding wide use in the stabilization of automotive gasolines was lignoresin anti-oxidant [67-69]. This anti-oxidant (GOST 3181-67) is produced from wood-chemical combines and today it is the fraction of the dry-distillation tar from mixed species of trees.

Table 71. Effectiveness of phenols from tar water as anti-oxidants in stabilizing gasolines of various origins (added to gasolines in the amount of 0.065 percent by weight)

Продукт 1	[illegible] 2		
	[illegible] 3	[illegible] 4	[illegible] 5
Бензин термического крекинга 6	145	275	510
Товарный бензин А-66 7	240	445	1000
неэтилированный 8			
этилированный 9	210	400	720
Бензин одноступенчатого каталитического крекинга 10	300	480 *	8[illegible]

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*Anti-oxidant concentration -- 0.05 percent.

Key:
1 -- Product
2 -- Induction period, minutes
3 -- without anti-oxidants
4 -- containing lignoresin anti-oxidant
5 -- containing phenols from semicoking
6 -- Thermal cracking gasolines
7 -- A-66 commercial gasolines
8 -- nonethyl
9 -- ethyl
10 -- Gasoline from single-stage catalytic cracking

Lignoresin anti-oxidant is added to gasoline in the amount of 0.065--0.1 percent. Laboratory studies, experimental storage, and tests in engines [75] showed that commercial lignoresin anti-oxidants can be used at a concentration of up to 0.13 percent in gasoline. Using this anti-oxidant concentration improves the chemical stability of gasoline and does not deteriorate its other operating properties.

In a study made of the effectiveness of lignoresin anti-oxidant at various concentrations [76], it was noted that the rate at which anti-oxidant is consumed during the oxidation of fuel depends on its initial concentration. The higher the initial concentration of the anti-oxidant, the higher the rate at which it is used up (Fig. 99). Experiments showed that adding the anti-oxidant to gasoline in portions is more effective than the single addition in the total amount.

The principle of multiple chemical stabilization is obviously more general and can be extended to other similar processes. If the rate of anti-oxidant consumption is proportional to its initial concentration, then

Table 72. Ability of anti-oxidants to be washed out with water and reduction in gasoline chemical stability when so treated (initial anti-oxidant concentration 0.065 percent)

Антиокислитель 1	Вымываемость антиокислителя водой, % 2	Индукционный период, мин 3	
		до промывки 4	после промывки 5
Древесносмольный 6	7,7	445	360
Фенолы из смолы полукоксования черемховских углей (фракция 210—330° C) 7	5,7	1050	800
Фенолы из подсмольных вод полукоксования черемховских углей 8	20,6	940	620

Key: 1 -- Anti-oxidant
2 -- Ability of anti-oxidant to be washed out with water
3 -- Induction period, minutes
4 -- before scrubbing
5 -- after scrubbing
6 -- Lignoresin
7 -- Phenols from the semicoking tar of Cheremkhovo coals (240-330° C fraction)
8 -- Phenols from the tar water from the semicoking of Cheremkhovo coals

one must assume that the continuous administration of an anti-oxidant in minimum doses required to prevent oxidation at a given instant would be most effective.

On the basis of these studies, a method [76] was developed for repeated chemical stabilization of automotive gasolines intended to be stored in severe conditions (vehicle fuel tanks, fuel lines, etc.). The method of repeated stabilization was tested in the experimental storage of gasolines. The results (Fig. 100) show the high effectiveness of this method even under unfavorable storage conditions in the southern climatic zone in the tanks of vehicles that had been placed in storage.

Commerical lignoresin anti-oxidant currently being produced is quite a broad fraction of wood tar from various species of trees. The stabilizing properties of this anti-oxidant are very low, since in addition to effective anti-oxidants it contains a considerable content of substances exhibiting only weak inhibiting properties. Among the latter are monomethyl esters of pyrogallol and their alkyl derivatives, and also the ethers of pyrocatechin and their homologs. Recently a commercially suitable method of converting these compounds into free polyphenols was found. When the vapor of lignoresin oils are passed through a tube heated to 500-550° C, the methoxyl and several hydroxyl groups of the phenols are cleaved. The vapor-phase pyrolysis leads to enriching lignoresin oils with monoatomic and free diatomic phenols.

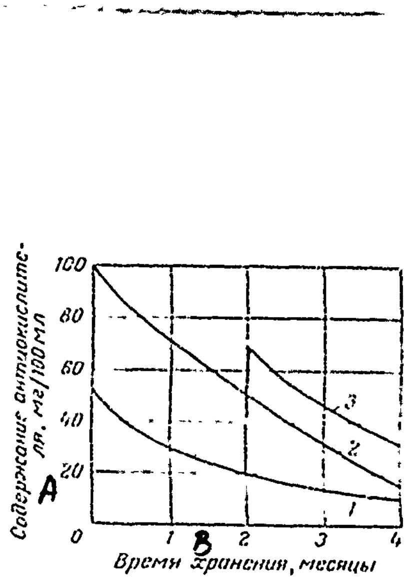


Fig. 99. Change in content of lignoresin anti-oxidant upon the storage of thermal-cracking gasoline:
1 — Gasoline with initial anti-oxidant content of 50 mg/100 ml
2 — Gasoline with initial anti-oxidant content of 100 mg/100 ml
3 — Gasoline with initial anti-oxidant content of 50 mg/100 ml and with the later addition of another 50 mg/100 ml
Key: A — Content of anti-oxidant, mg/100 ml
B — Storage time, months

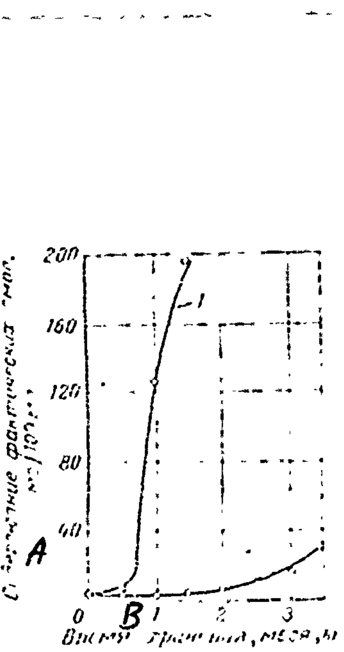


Fig. 100. Results of experimental tests of the effectiveness of additional stabilization when automotive gasoline was stored in the southern climatic zone:
1 — Initial gasoline
2 — Gasoline additionally stabilized during storage.
Key: A — Content of existent gums, mg/100 ml
B — Storage time, months

The pyrolysis of lignoresin oils was developed initially to produce a binder required in forming wood boards from wastes of wood processing enterprises (shavings, sawdust, etc.). However, this use of the composition of lignoresin oils, judging from the studies made on anti-oxidants prepared from the tars of the semicoking of coals, must lead to an improvement in anti-oxidizing properties.

The pyrolysate proved to be more effective than lignoresin anti-oxidant both in duration of induction period (Table 73), as well as in the inhibition of gum formation. The overall product of pyrolysis was found to be more effective; the pyrolysate fraction boiling above 235° C showed lower effectiveness.

The greatest effectiveness of the pyrolysate was observed when it was added to gasoline in concentrations up to 0.1 percent. At concentrations below 0.05 percent, the effectiveness of the pyrolysate decreases markedly, therefore the optimal range for the use of the pyrolysate must be regarded as concentrations from 0.05 percent to 0.1 percent. Effectiveness of the lignoresin anti-oxidant decreases sharply at concentrations below 0.05 percent. With the existing metering of lignoresin anti-oxidant (not more than 0.1 percent for the cracking component), the concentration of the anti-oxidant

Table 73. Effectiveness of pyrolysates of various origins as anti-oxidants (0.02 percent by weight concentration), in terms of induction period (minutes)

Антиокислитель 1	Окисленный бензин термического крекинга 2		Окисленный диизобутилен при 100° C 5
	при 100° C 3	при 110° C 4	
Не вводился 6	60	45	50
Товарный древесносмольный антиокислитель 7			
образец 1 8	410	185	210
образец 2 9	340	170	200
Пиролизат суммарный из масел смешанной смолы 10			
образец 1 8	460	—	345
образец 2 9 11	410	210	300
Пиролизат из масел смешанной смолы			
образец 1 8	425	—	340
образец 2 9	390	260	270

Key:
1 — Anti-oxidant
2 — Oxidized thermal cracking gasoline
3 — at 100° C
4 — at 110° C
5 — Oxidized diisobutylene at 100° C
6 — Was not added
7 — Commercial lignoresin anti-oxidant
8 — sample 1
9 — sample 2
10 — Composite pyrolysate from oils of mixed tar
11 — Pyrolysate from oils of mixed tar

in commercial automotive gasolines often proves to be lower than 0.05 percent. The effectiveness of the anti-oxidant at these concentrations is sharply reduced; the chemical stability of gasolines drops off. These results show that the concentration of anti-oxidants of lignoresin origin in commercial automotove gasolines must not be less than 0.05 percent.

Data of laboratory studies on the high effectiveness of the pyrolysate were completely confirmed by experimental-storage results. The pyrolysate was accepted for use as an anti-oxidant in automotive gasolines [77].

Compounds of the phenolic, amine, and aminophenolic types. In the technical mixtures of phenols which were discussed in the previous sections metal compounds have the same anti-oxidizing properties. Some of them are fillers, only adding to the concentration of the anti-oxidants used. From this standpoint, individual compounds are of special interest for use as anti-oxidants in gasolines. It is precisely these compounds that are gaining growing acceptance in the foreign practice of the chemical stabilization of automotive gasolines. In recent years, results have also been

Table 74. Effect of anti-oxidants on the oxidation induction period of gasolines

Антиокислитель 1	Концентрация, *мг*/100 *мл* 2	3 Индукционный период, мин	
		без антиокислителя 4	с антиокислителем 5
Бензил-*п*-аминофенол 6	10	265	[illegible]
α-Нафтол 7	10	265	[illegible]
Ди-*трет*-бутилкрезол 8	25	265	500
Тормозной препарат 9	50	265	525
Фенил-α-нафтиламин 10	25	305	485
п-Оксидифениламин 11	10	305	700
2,4-Диаминодифениламин 12	10	290	150
4,4-Дифенил-*п*-фенилендиамин 13	10	290	605

Key: 1 -- Anti-oxidant
2 -- Concentration, mg/100 ml
3 -- Induction period, minutes
4 -- without anti-oxidant
5 -- containing anti-oxidant
6 -- Benzyl-p-aminophenol
7 -- α-Naphthol
8 -- Di-ter-butylcresol
9 -- Commerical preparation
10 -- Phenyl-alpha-naphthylamine
11 -- p-Hydroxydiphenylamine
12 -- 2,4-Diaminodiphenylamine
13 -- 4,4-Diphenyl-p-phenylenediamine

Table 75. Effectiveness of phenylaminediamines as anti-oxidants for thermal cracking gasoline

Антиокислитель 1	Поглощение кислорода за 5 ч окисления при 100° С, *мл* 2	Кислотность бензина после окисления, *мг* КОН/100 *мл* 3	[illegible] 4
о-Фенилендиамин 5	66	51,0	0,16
м-Фенилендиамин 6	125	51,9	0,21
п-Фенилендиамин 7	10	0,7	0,12
п-Оксидифениламин 8	2	0,1	0,05

Key: 1 -- Anti-oxidant
2 -- Absorption of oxygen after 5 hours of oxidation at 100° C, ml
3 -- Acidity of gasoline after oxidation, mg KOH/100 ml
4 -- Optical density of gasoline after oxidation
5 -- o-Phenylenediamine
6 -- m-Phenylenediamine
7 -- p-Phenylenediamine
8 -- p-Hydroxydiphenylamine

published in our country concerning the use of individual chemical compounds as anti-oxidants [66, 78]. However, thus far they have not found wide acceptance in automotive gasolines.

The results of rating the effectiveness of the most diverse individual chemical compounds which could have anti-oxidant properties based on their structure, or else which were used or tested as anti-oxidants in related areas of technology are given in Fig. 101 and Tables 74 and 75.

Among the individual chemical compounds are some which reveal high anti-oxidizing properties in gasolines, at extremely low concentrations. The dependence of the oxidation inducation period of gasolines on anti-oxidant concentrations within the limits studied is linear. Of the compounds tested, p-hydroxydiphenylamine exhibits the best anti-oxidizing properties.

Laboratory findings were completely corroborated also by the results of the experimental storage of gasoline in the fuel tanks of vehicles kept in storage (Fig. 102). It was found that the p-hydroxydiphenylamine concentration in gasolines must not exceed 0.015-0.020 percent. At higher anti-oxidant concentrations (for example, 0.024 percent), gasoline stability not only does not rise, but even decreases somewhat (cf. curve 3 in Fig. 102). The results of storage recommend p-hydroxydiphenylamine as an anti-oxidant for automotive gasolines. At the present time, some oil refineries in the country use p-hydroxydiphenylamine in the chemical stabilization of automotive gasolines. This compound stabilizes not only gasoline hydrocarbons, but also tetraethyl lead present in the fuel [79, 80].

Metal deactivators

All fuels come into contact with metals during transportation, pumping, and storage. Most equipment for transporting and storing petroleum products is made of steels of various grades; small parts, some auxiliary equipment, and the feed systems of engines are made of alloys which also include non-ferrous metals in their compositions. Metals can be contained in gasoline in a dissolved form, even though at very low concentrations. Metal can enter a gasoline directly from the crude as it is being refined or from contact with metal equipment and containers. Residues of chemical reagents used in secondary refining processes can also be a cause of traces of metals appearing in gasolines. And, finally, some metals bound in organometallic compounds are specifically added to fuels to enhance their operating properties.

Most metals have the ability to catalytically accelerate oxidative processes, thus causing the premature spoilage of automotive gasolines.

The catalytic action of metals on fuels in their oxidation was investigated by P. P. Trep'yakov, I. Ye. Bespolov, R. S. Mindlin, M. B. Vol'f and O. V. Vasil'yeva, F. B. Dauning, Ts. Ye. Pedersen, Ye. L. Val'ters et al. [81-85]. I. Ye. Bespolov [81] investigated the role of the carburetor bowl

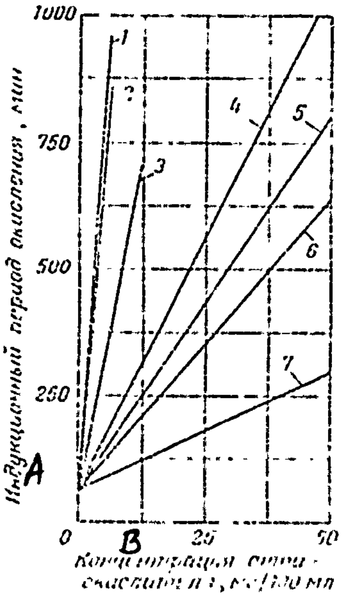


Fig. 101. Effect of anti-oxidant concentration on the oxidation induction period of thermal cracking gasoline:

1 -- p-hydroxydiphenylamine
2 -- benzyl-p-aminophenol
3 -- phenyl-alpha-naphthylamine
4 -- 2,4-dimethyl-6-tei-butylphenol
5 -- Commercial preparation (CP)
6 -- Lignoresin anti-oxidant
7 -- Neozone D (anti-oxidant for rubber)

Key: A -- Oxidation induction period, minutes
B -- Anti-oxidant concentration, mg/100 ml

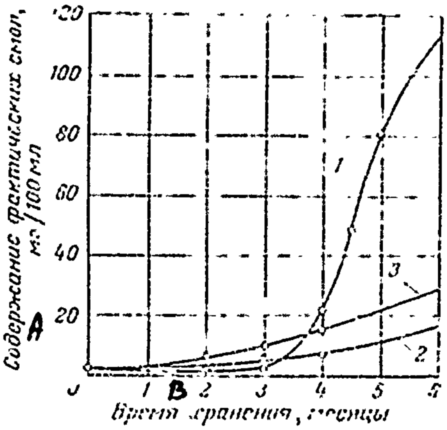


Fig. 102. Effect of concentration of p-hydroxydiphenylamine on the stability of thermal cracking gasoline in storage:

1 -- Initial gasoline
2 -- Gasoline containing 0.008 percent p-hydroxydiphenylamine
3 -- gasoline containing 0.024 percent p-hydroxydiphenylamine

Key: A -- Content of existent gums, mg/100 ml
B -- Storage time, months

material on the oxidation of cracking gasoline showing the gum residue was determined by the standard so-called "copper cup" method. He found that the highest gum content is formed in a copper cup. R. S. Mindlin [81] investigated the effect copper has on the oxidation of gasoline in glass bottles.

M. V. Vol'f and O. V. Vasil'yev [83] showed that when gasoline stabilized with alpha-naphthol is stored, a loose deposit of ferric naphtholate forms in the presence of iron, and because of this gasoline stability falls off sharply.

The effect of copper compounds on the oxidation of purified cracking gasolines was investigated by Dauning [84]. Val'ters [82] showed that the catalytic activity of copper alloys is proportional to their copper content. Pedersen [85] studied the effect of the copper concentration on the chemical stability of thermal cracking gasolines after sulfuric acid scrubbing. Results were published from studies of the effect that metals such as steel, copper, brass, lead, tin, aluminum, and zinc have on gasolines differing in chemical stability [86, 87].

As follows from the data in Table 76, in the presence of metals, the induction period of gasoline oxidation is shorter.

Copper has the strongest catalytic effect. It shortens the induction period by 70-80 percent. Brass shows a somewhat lower catalytic activity. In its presence [text pages 244-245 are missing]....

Then, on exposure to temperature and oxidation in the presence of metals, solid compounds that are hard to remove are formed from the liquid gums. The formation of these deposits in fuel lines, stopcocks, channels, and jet nozzles of carburetors alters their cross section and causes disturbances in engine operation.

Gum compounds can precipitate from a gasoline solution for the following reasons:

as the result of chemical transformations of primary oxidation products (as a rule, dissolved in hydrocarbons) gum compounds that are insoluble in gasolines are formed;

the content of gums formed in gasoline exceed their solubilities and the excess gums precipitate as a second phase;

gums dissolved in gasoline are polar compounds; they are adsorbed on the walls of pipelines, forming a layer of gum compounds.

When automotive gasolines are in use, the precipitation of gums evidently is a consequence of all these three above-listed causes.

Experiments using gasoline containing different gum concentrations were conducted in studying the formation of gum deposits on various metal surfaces (Table 78).

Three strips -- copper, brass, and steel -- were suspended on glass hooks in each bottle containing gasoline. The gasoline was stored in a thermostat at 40° C for 45 days. As we can see from Table 78, the gum content on these strips depends on the gum content in gasolines and on the kind of metal. As the existent gum content in a gasoline was increased, the amount of deposits on the strips rose appreciably. Significantly heavier deposits were formed on brass and copper strips than on steel.

The amount of deposits depends to a large extent on the content of mercaptan sulfur. When mercaptan is present, and given an elevated temperature (70° C), the difference in the effect of copper and steel strips decreases appreciably (Table 79). The addition of mercaptans especially sharply increases the amount of deposits formed on steel strips, however even in these conditions the amount of deposits on copper and brass remains higher than on steel. The content of deposits depends on the structure of the mercaptans.

The relatively small number of mercaptans studied does not provide categorical conclusions as to how their structure affects the amount of deposits. However, it must be assumed that aromatic mercaptans give a lower deposit content than aliphatic. With increase in molecular weight, the effect of aliphatic mercaptans is intensified. Aliphatic mercaptans of iso-structure evidently promote the formation of deposits to a greater extent than normal-structure mercaptans, including also secondary mercaptans.

Table 78. Effect of gums in thermal cracking gasoline* on deposit formation on metal plates

Содержание фактических смол, мг/100 мл 1		2 Количество отложений, г/м²		
до начала хранения 3	после хранения 4	на стали 5	на латуни 6	на меди 7
4,6	12,2	6,1	10,2	8,0
8,6	12,0	4,9	7,4	8,8
17,8	41,2	6,8	18,5	10,8
28,0	50,0	10,4	24,2	24,5
60,0	132,8	16,8	46,8 **	44,3
98,0	140,0	12,2	41,0 **	48,8 **

---

* Mercaptan sulfur content in gasoline was 0.0102 percent.

** Some of the liquid gums fell from the plate onto the bottom.

Key:
1 — Existent gum content, mg/100 ml
2 — Amount of deposits, g/m^2
3 — before beginning of storage
4 — after storage
5 — on steel
6 — on brass
7 — on copper

Thus, the formation of deposits on the walls of fuel lines, carburetors, gasoline pumps, and other parts of the vehicle fuel feed system depends on the content of gums in the gasoline and on the content and structure of mercaptans.

When ethyl automotive gasolines are stored, tetraethyl lead can decompose and affect oxidation and gum formation. Tetraethyl lead in automotive gasolines, when unsaturated hydrocarbons are present, behave differently than in aviation gasolines. When ethyl aviation gasolines are stored, first deposits of lead compounds are formed; here the gum content does not yet reach the maximum allowable levels. When ethyl automotive gasolines are stored, accelerated gum formation occurs first of all, and the lead deposit forms at more profound stages of oxidation.

M. B. Vol'f showed that the addition of ethyl fluid to thermal cracking gasoline lowers the oxidation induction period by 60-90 minutes and that the decomposition of TEL in gasolines containing unsaturated hydrocarbons occurs more intensively than in straight-run gasolines. Val'ters et al. [89]

Table 79. Effect of organic sulfur compounds on the amount of deposits on metal plates (oxidation at 70° C for 70 hours)

Образец 1	Содержание серы, % 2		Количество отложений, г/м² 3		
	общей 4	меркаптановой 5	на стали 6	на латуни 7	на меди 8
Бензин каталитического крекинга 9	0,12	0,0077	0,6	1,2	0,8
Бензин термического риформинга 10	0,21	0,0267	21,2	30,2	24,1
Бензин термического крекинга 11	0,20	0,0102	7,3	15,8	8,6
Тот же бензин с добавлением: 12					
н-октилмеркаптана 13	0,25	0,0595	16,8	31,7	28,6
втор-октилмеркаптана 14	0,21	0,0584	18,5	[illegible]	20,9
трет-октилмеркаптана 15	0,26	0,0591	30,6	22,4	37,6
пропилмеркаптана 16	0,25	0,0580	16,9	22,0	21,1
изоамилмеркаптана 17	0,24	0,058[illegible]	26,8	37,9	37,9
гексилмеркаптана 18	0,26	0,0610	27,2	30,7	19,3
бензилмеркаптана 19	0,24	0,0583	15,0	16,6	16,8
фенилэтилмеркаптана 20	0,25	0,0589	14,0	19,8	15,[illegible]

Key:
1 -- Sample
2 -- Sulfur content
3 -- Amount of deposits, g/m^2
4 -- total
5 -- mercaptan
6 -- on steel
7 -- on brass
8 -- on copper
9 -- Catálytic cracking gasoline
10 -- Thermal reforming gasoline
11 -- Thermal cracking gasoline
12 -- Gasoline as above, with the addition of the following
13 -- p-octylmercaptan
14 -- sec-octylmercaptan
15 -- ter-octylmercaptan
16 -- propylmercaptan
17 -- isoamylmercaptan
18 -- hexylmercaptan
19 -- benzylmercaptan
20 -- phenylethylmercaptan

maintain that the effect of TEL on the oxidation of gasolines rich in unsaturated hydrocarbons is slight. S. E. Kreyn [90] showed that TEL somewhat accelerates the oxidation of hydrocarbons such as tetralin and mesitylene, and has practically no effect on the oxidation of isodecane and p-cymene. K. I. Ivanov et al. [91] noted that tetrahydronaphtyl hydroperoxide formation is accelerated, and, especially, undergoes decomposition in the presence of TEL.

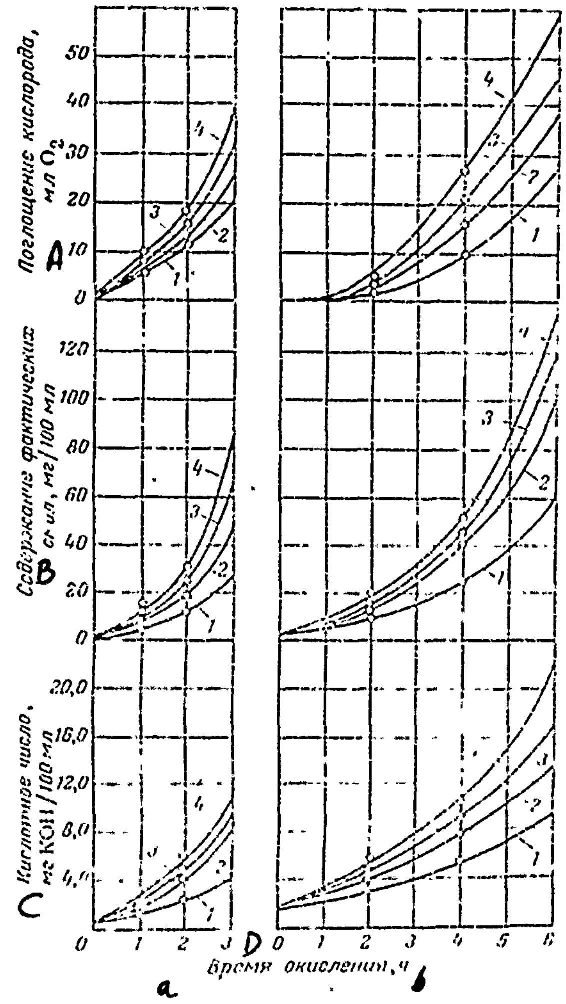


Fig. 103. Effect of TEL on the oxidation of unstabilized automotive gasoline (a) and gasoline containing antioxidant in the amount of 50 mg/100 ml (b) at 100° C:

1 — Gasoline containing no TEL
2 — Gasoline containing 0.41 g TEL/kg
3 — Gasoline containing 0.82 g TEL/kg
4 — Gasoline containing 1.23 g TEL/kg

Key: A — Oxygen absorption, ml O_2
B — Existent gum content, mg/100 ml
C — Acid number, mg KOH/100 ml
D — Oxidation time, hours

Fig. 103 presents [79] the results of oxidizing thermal cracking gasoline with various tetraethyl lead content (TEL content in R-9 fluid is 50 percent).

In evaluating the effect of TEL on gasoline oxidation, one must bear in mind that in this case oxygen is used up not only in oxidizing fuel hydrocarbons, but also in oxidizing the TEL as such. Therefore a fuller pattern of the effect of TEL can be obtained by comparing the oxygen adsorption curves with the curves describing the change in the existent gum content and in acidity. The data presented (Fig. 103) indicates that TEL accelerates gasoline oxidation.

Similar results were also obtained in conditions of actual gasoline storage in the central climatic zone (Fig. 104). The presence of TEL causes intensified gum formation and a rise in the acidity of gasoline; the allowable storage time for gasoline is shortened by roughly 20 percent.

Decomposition of TEL with the formation of lead sediment occurs also when ethyl gasolines containing unsaturated hydrocarbons are oxidized. But TEL decomposition occurs nearly simultaneously with the onset of intense gum formation. Precipitates of lead compounds are detected in the gasoline samples in which the gum content already exceeds the allowable norm.

One must notice yet another feature of ethyl gasolines. The effect of sunlight accelerates the oxidation of gasoline and TEL. But the extent of the action of light on TEL is obviously higher than in gasolines Therefore in ethyl gasolines subjected to sunlight, primarily TEL is oxidized, and the precipitate of lead compounds appears very rapidly. We can assume that the oxidation of hydrocarbons and nonhydrocarbon impurities in this case is somewhat inhibited because TEL and its decomposition products react more intensively with oxigen and peroxides under the effect of light. The decomposition of peroxide compounds rupture the reaction chains and slow down gum formation.

In conditions of ordinary storage in use, ethyl gasolines are not subject to sunlight, however this phenomenon can occur in the glass cylinders of gasoline pumps where gasoline can be "irradiated" for sometime interval.

Catalytic action of metals and the consumption rate of anti-oxidants. In a study of the catalytic effect of metals on the oxidation of automotive gasolines, it was noted that anti-oxidant consumption rises markedly when metals are present. The rate of anti-oxidant consumption is directly proportional to the catalytic activity of a metal. Earlier it was already stated that the greatest acceleration in oxidation was observed in the presence of copper and brass; it is precisely in the presence of these metals that the most rapid consumption of anti-oxidant is noted (Fig. 105). The rate of anti-oxidant consumption when gasolines are oxidized in the presence of other metals also approximately corresponds to their catalytic activity.

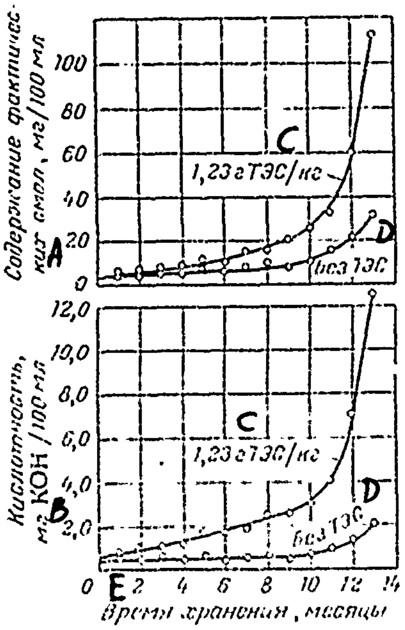


Fig. 104. Effect of tetraethyl lead on the oxidation of commercial automotive gasoline in storage conditions at ambient air temperatures in the central climatic zone

Key: A — Existent gum content, mg/100 ml
B — Acidity, mg of KOH/100 ml
C — 1.23 g TEL/kg
D — Not containing TEL
E — Storage time, months

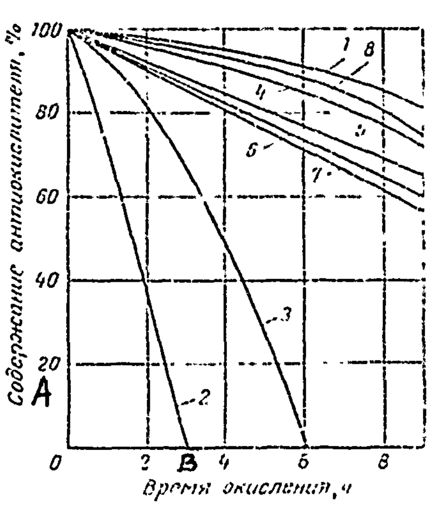


Fig. 105. Change in anti-oxidant content when fuel is oxidized in the presence of metals:

1 — Not containing metal
2 — Containing copper
3 — Containing brass
4 — Containing iron
5 — Containing aluminum
6 — Containing zinc
7 — Containing tin
8 — Containing lead

Key: A — Anti-oxidant content
B — Oxidation time, hours

In experiments on individual hydrocarbons in gasolines devoid of natural anti-oxidants after the latter were filtered through aluminum oxide, it was established that in the absence of anti-oxidants metals do not accelerate hydrocarbon oxidation. These results suggest that the accelerated oxidation of commercial fuels in the presence of metals is accounted for by the rapid consumption of the anti-oxidant. The consumption of the anti-oxidant is evidently caused by the direct action of the metal on the anti-oxidant; and here the nature of the effect can vary. For example, Kreulen [92] maintains that the oxidation duration period of white oils is shortened in the presence of copper because anti-oxidants are adsorbed onto the metal and cease to inhibit the oxidation period. Yu. S. Zaslavskiy,

S. E. Kreyn, R. N. Shneyerova, and G. I. Shor [93] showed that similar additives, in the formation of a protective film, can react directly with the metal.

Pedorsen [85] suggested the following mechanism for the catalytic action of copper in the oxidation of fuels. The reaction between peroxides and the anti-oxidant is greatly accelerated when copper is present, while this reaction proceeds relatively slowly in ordinary conditions. Metallic or monovalent copper has a catalytic effect; as a result of the reaction, divalent copper is formed, exhibiting no catalytic properties. Divalent copper is reduced down to monovalent in the presence of an anti-oxidant, and the catalytic action of copper is renewed. In the absence of an anti-oxidant, divalent copper accumulates in gasoline, and is not reduced, and therefore it is not observed to have a catalytic effect.

It can be assumed that the direct accelerating effect of metals on the oxidation of the anti-oxidant as such is most probable. We know that only products which can themselves be oxidized by air oxygen exhibit anti-oxidant properties. In the presence of metals the rate of anti-oxidant oxidation evidently is sharply increased, which then leads to its rapid consumption. However, additional studies are needed for a definitive judgment.

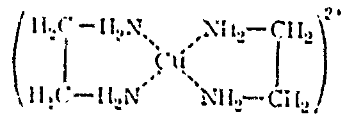
Characteristics of the use of deactivators. To prevent the catalytic effect of metals on products such as hydrogen peroxide, certain vitamins, animal and vegetable fats, plant juices, rubber, certain synthetic fibrous materials, photographic reagents, perfumes, drugs, etc., special additives are used successfully, referred to as metal deactivators (inactivators) [94, 95].

Work on the use of deactivators as fuel additives began because the very rapid oxidation of cracking gasolines purified with copper salts was noted. Traces of copper remaining in gasoline after scrubbing caused intense gum formation, deterioration of gasoline color, etc. [84, 96, 97]. Initially investigators tried to find methods to completely remove the traces of copper from the gasoline. Various ways of extracting the copper were studied, but they all required special equipment, involved a large consumption of reagents, and did not always completely remove the traces of copper.

In 1939 the first paper on deactivating additives preventing the catalytic effect of solute copper on gum formation in gasolines was published [84]. The authors of this study showed that the mechanism of action of metal deactivators differs fundamentally from the mechanism of ordinary anti-oxidants. It is sufficient to state that an effective deactivator cannot, generally, exhibit anti-oxidizing properties. Based on a limited number of foreign studies, the following mechanism of deactivator action can be proposed [94]. When gasolines undergo oxidation in the presence of metals, homogeneous catalysis occurs, and the metal exerting the catalytic effect is in the ionic state. The action of compounds suppressing the catalytic activity of the metal is due to the fact that they exhibit the ability to form complex compounds of a nonionic type with the metal ions. These complexes have not catalytic effect and therefore do not cause accelerated oxidation.

The ability of organic products to form complex compounds with metals has been known for a long time. However, the diversity of their practical use as metal deactivators for fuels of petroleum origin have raised a number of new, independent theoretical problems. We know that the simplest organic compounds containing even a single hetero-atom (nitrogen, oxygen, sulfur, or phosphorus), have coordination bonds and are capable of forming complex compounds with copper, but these compounds have low stability and in their presence the catalytic effect of copper on gasoline oxidation persists.

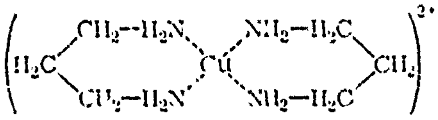
Organic compounds containing two hetero-atoms form more stable complexes, since the coordination bonds of hetero-atoms, on being completed at the metal, form unique rings exhibiting some strength. For example, ethylenediamine forms with copper a complex of the following type:



As the result of the closure of coordination bonds of terminal hetero-atom, two five-membered rings are formed. Compounds of this type exhibit greater effectiveness than compounds containing a single hetero-atom, and in their presence the catalytic effect of copper on gasoline oxidation is significantly reduced.

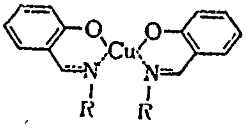
The strength of a complex compound depends on precisely what hetero-atom participates in the coordination bond. For example, nitrogen forms stronger coordination bonds, and oxygen -- less strong [97].

By closure of the terminal atoms in a complex compound, not only can five-membered rings be formed, but also rings with a larger number of atoms. For example, diaminopropane yields with copper a complex compound with six-membered rings:

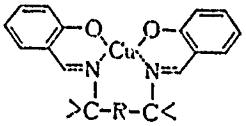


A study [97] showed that compounds forming rings of five or six atoms exhibit the highest deactivating ability. The strength of a complex compound, in addition to the number of bonds, depends also on the number of rings formed by a given compound when it complexes with copper. A larger number of rings means greater strength of a complex. The most effective metal deactivators found among compounds that form so-called chelate salts with metals. In these compounds one hetero-atom is bonded with a metal by an ionic bond, and the other closes the chelate ring with a coordination bond.

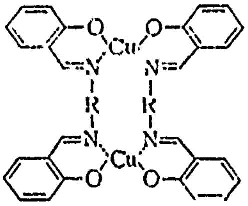
Pedersen [85], on studying various compounds as metal deactivators, found that chelate salts with copper can be of the following three types:



Type 1



Type 2



Type 3

The compounds studied, forming with copper chelate salts of type 2, proved to be the most effective deactivators. Compounds forming complexes of type 1 and 3 have lower deactivating properties. Actually, a complex compound of specifically type 2 must have the greatest stability, since it has the larger number of chelate rings (three). A type 3 complex compound also has three rings about the carbon atom, but the central ring is composed of more than eight atoms, and the presence of this ring does not promote an increase in complex stability.

For any compound to be used as a metal deactivator in the conditions of gasoline oxidation, it must meet the following requirements: have a tendency to complexate with metals; bond all available ions of a given metal as fully as possible; combine into complex compounds as many metals as possible; that is, the general; form complex compounds soluble in fuel; and, finally, meet all the general requirements imposed on gasoline additives (inability to be washed out with water, combustion without forming deposits, stability in storage, availability, etc.).

The largest number of products exhibiting deactivating properties are found among compounds of the Schiff's base class -- products of the condensation of amines and aromatic aldehydes. High deactivating properties were found for disalicylidene ethylenediamine and salicylidene-o-aminophenol. Of compounds in other classes, 5,7-dibromo-8-hydroxyquinoline exhibits high effectiveness (Fig. 106).

The data in Fig. 106 show the high effectiveness of metal deactivators. Gasoline containing anti-oxidants in the presence of metals is subjected to very rapid oxidation. Small additions of deactivators (0.015 percent) make it possible to significantly increase the chemical stability of gasoline.

The effectiveness of a deactivator depends on its concentration in gasoline. At its optimal concentration, a deactivator protects the anti-oxidant against accelerated consumption in the presence of metal, but in so doing the overall stability of the metal is determined by the effectiveness of the anti-oxidant. Fig. 107 presents the results of a study of what effect the metal deactivator concentration (disalicylidene ethylenediamine) has on the stability of thermal cracking gasoline containing pyrolysate -- the upper curve, and on the stability of thermal cracking gasoline containing p-hydroxydiphenylamine -- the lower curve. A comparison of the trend of these curves in Fig. 107 shows that the anti-oxidant that is more effective in the absence of metal remains more effective even when a metal strip is present and at the optimal deactivator concentration.

Similar results can be seen also in Fig. 106. Gasoline containing ionone is less stable than gasoline containing p-hydroxydiphenylamine, either without an activator or even in the presence of all the metal deactivators tested.

For the chemical stabilization of gasolines, an effective anti-oxidant must be used simultaneously with an effective deactivator. Using a metal deactivator as a gasoline additive does not reduce the requirements imposed on the anti-oxidant's effectiveness. When p-hydroxydiphenylamine is used at a 0.01 percent concentration, the optimal deactivator concentration is also 0.01 percent. In other words, the optimal ratio of disalicylidene ethylenediamine and p-hydroxydiphenylamine is 1:1. It is at precisely this ratio that a test was made of the effectiveness of the blend of anti-oxidant and deactivator as a function of its concentration. The findings (Fig. 108) show that the total content of p-hydroxydiphenylamine and disalicylidene ethylenediamine must not exceed 0.02-0.03 percent. The effectiveness of deactivators when oxidation occurs in the presence of a copper strip is more than twice the anti-oxidant's effectiveness (cf. Fig. 108).

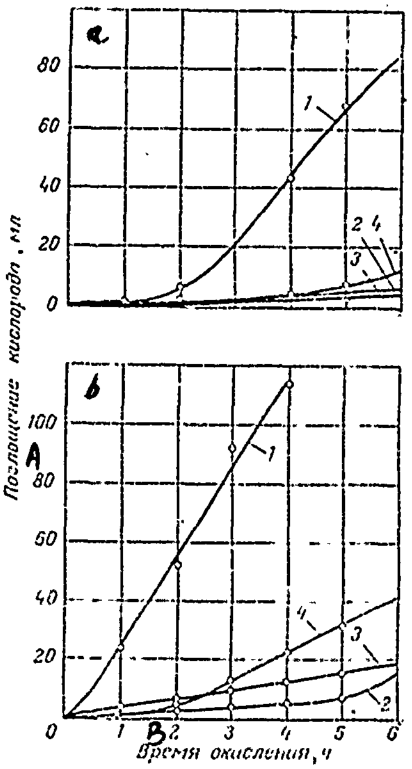


Fig. 106. Relative effectiveness of metal deactivators in gasoline containing various anti-oxidants — p-hydroxydiphenylamine (0.015 percent) (a) and ionone (0.03 percent) (b):

1 — Without deactivator
2 — Containing disalicylidene ethylenediamine (0.015 percent)
3 — Containing salicylidene aminophenol (0.015 percent)
4 — Containing 5,7-dibromo-8-hydroxyquinoline (0.015 percent)
Key: A — Oxygen absorption, ml
B — Oxidation time, hours

In Fig. 108, curve 1 characterizes the oxidizability of gasoline containing a deactivator in the absence of an anti-oxidant. The results show that the deactivator itself has extremely low anti-oxidizing properties. Similar data on the anti-oxidizing properties of salicylidene-o-aminophenol were obtained in an induction period determination:

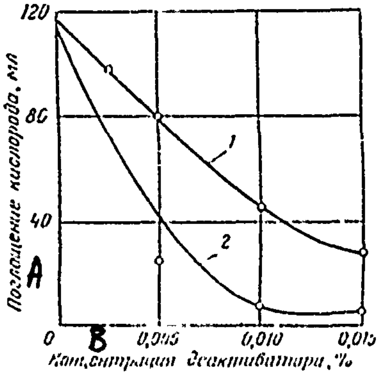


Fig. 107. Effectiveness of disalicylidene ethylenediamine in gasoline containing various anti-oxidants; oxidation for 5 hours at 110° C:

1 -- Gasoline containing pyrolysate (0.05 percent)
2 -- Gasoline containing p-hydroxydiphenylamine (0.01 percent)

Key: A -- Oxygen absorption, ml
B -- Deactivator concentration

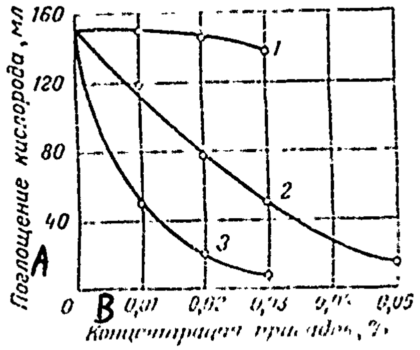


Fig. 108. Effect of additives on the oxidizability of thermal cracking gasoline using a copper strip at 110° C for 6 hours:

1 -- Metal deactivator (disalicylidene ethylenediamine)
2 -- Anti-oxidant (p-hydroxydiphenylamine)
3 -- Metal deactivators + anti-oxidant in a 1:1 ratio

Key: A -- Oxygen absorption
B -- Additive concentration

Deactivator concentration, percent	Induction period, minutes
0	345
0.010	390
0.015	415

Thus, metal deactivators, exhibiting very low anti-oxidizing properties, can be used only in combination with anti-oxidants. In this case the anti-oxidant imparts high chemical stability to the gasoline, while the deactivator prevents the accelerated consumption of the anti-oxidant by the catalytic action of metals, thus significantly enhancing the overall effect by suppressing the anti-oxidant.

One of the main requirements imposed on a metal deactivator is that it be able to combine into complex compounds the ions of all metals with

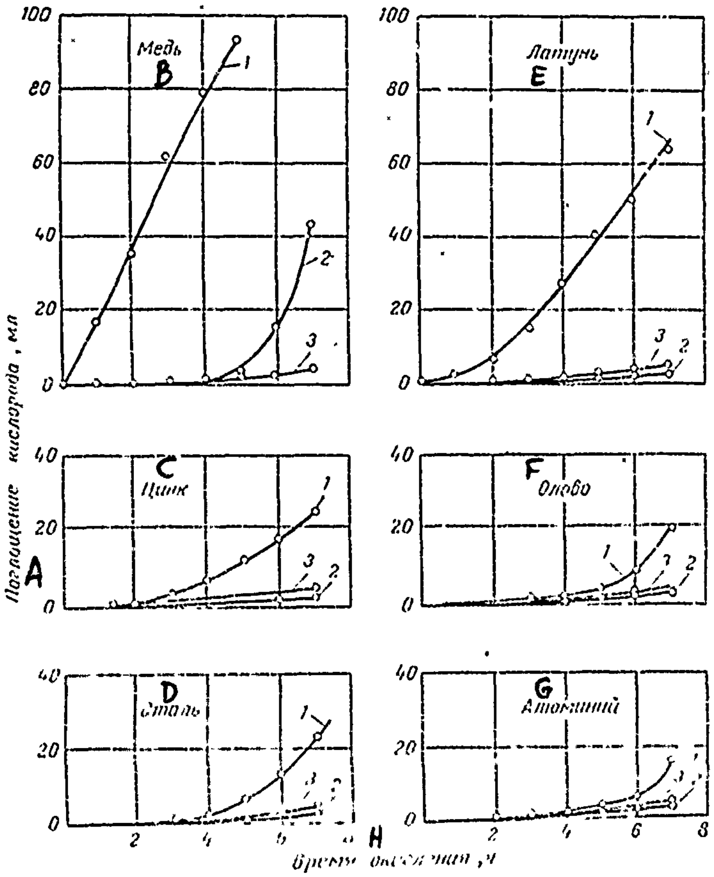


Fig. 109. Effectiveness of disalicylidene ethylenediamine in suppressing the catalytic effect of metals on thermal cracking gasoline stabilized with 0.01 percent p-hydroxydiphenylamine to which 0.01 percent deactivator was added; oxidation at 110° C:

1 -- Containing metal, but without deactivator
2 -- Containing metal and deactivator
3 -- Without metal and deactivator

Key: A -- Oxygen absorption, ml
B -- Copper
C -- Zinc
D -- Steel
E -- Brass
F -- Tin
G -- Aluminum
H -- Oxidation time, hours

Table 80. Effect of deactivator — disalicylidene ethylenediamine (0.01 percent) on the oxidizability of thermal cracking gasoline containing p-hydroxydiphenylamine (0.01 percent) in the presence of various metals (oxidation at 110° C for 7 hours)

Образец бензина 1	2 Содержание смолистых веществ в продуктах окисления, мг/100 мл		5 Кислотность мг КОН/100 мл
	3 растворимых в бензине	4 нерастворимых в бензине	
С медью 6	656	109	69,2
С медью и деактиватором 7	358	21	32,8
С латунью 8	608	83	66,0
С латунью и деактиватором 9	117	0	2,4
Со сталью 10	166	6	7,3
Со сталью и деактиватором 11	124	0	1,7
С алюминием 12	203	0	17,3
С алюминием и деактиватором 13	104	0	2,8
С цинком 14	417	45	41,5
С цинком и деактиватором 15	140	0	1,7
С оловом 16	269	9	20,7
С оловом и деактиватором 17	68	0	1,7

Key: 1 -- Gasoline sample
2 -- Gum content in oxidation products, mg/100 ml
3 -- soluble in gasoline
4 -- insoluble in gasoline
5 -- Acidity, mg KOH/100 ml
6 -- Containing copper
7 -- Containing copper and deactivator
8 -- Containing brass
9 -- Containing brass and deactivator
10 -- Containing steel
11 -- Containing steel and deactovator
12 -- Containing aluminum
13 -- Containing aluminum and deactivator
14 -- Containing zinc
15 -- Containing zinc and deactivator
16 -- Containing tin
17 -- Containing tin and deactivator

which gasoline comes into contact during storage, transportation, and use. Results of studies showed that metal deactivators such as salicylidene-o-aminophenol, disalicylidene ethylenediamine, and several others are capable of suppressing the catalytic action of copper, brass, steel, tin, zinc, aluminum, and other metals.

Adding a deactivator reduces the amount of oxygen absorbed during oxidation (Fig. 109), lowers the content of oxidation products in the presence of all the metals tested (Table 80), and restores the oxidation induction period (Table 81).

Table 81. Effect of salicylidene-o-aminophenol (0.01 percent) on the oxidation induction period of gasolines in the presence of various metals

Металл 1	Индукционный период, мин 2		
	без металла 3	с металлом 4	с металлом и деактиватором 5
Медь 6	345	85	280
Латунь 7	340	120	325
Сталь 8	540	420	525
»	340	240	350
Цинк 9	410	360	405
Олово 10	615	500	600
Алюминий 11	390	350	405
»	290	210	285

Key:
1 -- Metal
2 -- Induction period, minutes
3 -- without metal present
4 -- with metal present
5 -- in the presence of metal and deactivator
6 -- Copper
7 -- Brass
8 -- Steel
9 -- Zinc
10 -- Tin
11 -- Aluminum

[Text pages 258-259 are missing.]. . . . . . .

...results show that a metal deactivator slows down oxidation processes in ethyl gasoline. A heavy precipitate of lead compounds is formed in a gasoline containing no deactivator, in 4 hours of oxidation at 110° C, while the ethyl fluid content is reduced from 4.1 to 2.97 ml/kg. The ethyl fluid content remains unchanged in a gasoline containing a deactivator in the same conditions, no precipitate is observed to form, and oxygen absorption does not occur.

Similar results were obtained also in an experimental storage of gasoline samples in a thermostat at 50° C. Even after one month's storage, in a gasoline containing no deactivator a precipitate of TEL decomposition products was formed, and the octane number of this fuel was reduced by 1.5 points. No precipitate formation or reduction in knock resistance was observed for a period of 10 months in a gasoline containing a deactivator.

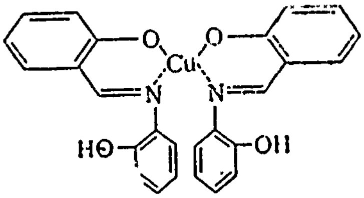
The presence of a deactivator in gasoline does not diminish the effectiveness of TEL as an antiknock. Thus, a test made of the octane numbers of samples of a gasoline containing different deactivator contents showed that the octane number of ethyl gasoline does not change from the suppression of the deactivator.

Thus, chemical stabilization by the combined addition of an anti-oxidant and deactivator gives additional advantages for ethyl gasolines, since it makes it possible to completely correct the decomposition of tetraethyl lead in storage [80, 98].

Effect of deactivator structure on its activity. We note from the theory of chelate compounds that in complexing with metals, rings consisting of five to six atoms are the most stable. Accordingly, in synthesizing Schiff's basis with good deactivating properties, only hydroxybenzaldehyde is suitable, with a hydroxy group in the ortho-position to the aldehyde group (salicylic aldehydes). Schiff's basis composed of m-p-hydroxybenzaldehydes are formed in the complexing of seven- and eight-membered rings, which do not have adequate stability. In other words, the selection of an aromatic aldehyde in the synthesizing of deactivators from the class of Schiff's basis is limited to a certain extent. The selection of an amine to synthesize a Schiff's base exhibiting good anti-deactivating properties is less restrictive, and amines of various structures have been composed for this purpose in the patent literature.

However, the results of studies (cf. Table 82) showed that the effectiveness of deactivators depends also on the structure of the aromatic amine [99]. Deactivating properties increase when a hydroxy group is introduced into the amine molecule and depend on the mutual position of the hydroxy and amine group, increasing from the meta to para and the ortho position. In contrast to anti-oxidants, the most active metal deactivators are compounds with constituents not in the para but in the ortho position.

Salicylidene hydroxyanilines yield with copper complexes of the following structure:



Evidently, the presence of the hydroxy group in the ortho position provides favorable conditions for the formation by nitrogen of a stronger coordination bond.

A similar dependence of effectiveness on structure was found also for disalicylidene phenylaminediamine*:

	Oxygen absorption, ml	Existent gum content after oxidation, mg/100 ml
Initial gasoline	0.5	10
Gasoline as above, in the presence of		
copper	22.3	66
copper and salicylidene-analine	20.1	60
copper and salicylidene-o-hydroxyanaline (salicylidene-o-aminophenol)	1.7	15
copper and salicylidene-m-hydroxyanaline (salicylidene-m-aminophenol)	18.1	43
copper and salicylidene-p-hydroxyanaline (salicylidene-p-aminophenol)	5.9	40
copper and disalicylidene-o-phenylenediamine	1.6	44
copper and disalicylidene-m-phenylenediamine	23.1	46
copper and disalicylidene-p-phenylenediamine	14.7	61

---

* Oxidation was carried out for 2 hours at 110° C.

Even in these the ortho position of the substitutents affected the deactivation ability.

So effective metal deactivators from the class of Schiff's basis can be found among compounds prepared with the participation of salicylic aldehyde or its homologs and an aromatic amine which has some substituent in the ortho position to the amine group.

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[To Chapter Six]

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CHAPTER SEVEN
GASOLINES AND ENGINE DEPOSITS

When automotive gasolines are used in engines, deposits are observed to form in the fuel feed system, intake manifold, and on the walls of the combustion chambers. To ensure automotive engine reliability and longevity, the gasolines must exhibit minimum tendency to form deposits. The ability of gasolines to form deposits in an engine is associated mainly with their chemical composition. The significance of individual groups of chemical compounds incorporated in gasolines in the deposit forming process varies and depends strongly on temperature conditions. Deposits in the fuel system and in the engine intake manifold are formed at moderate temperatures and in composition and properties differ considerably from high-temperature deposits on combustion chamber walls.

The tendency of gasolines to form deposits in engine combustion chambers is most significant in operating conditions.

Deposit Formation in Combustion Chambers

Deposit formation in combustion chambers causes a significant deterioration in the operating indicators of automotive carburetor engines. As a result of deposits forming, engine efficiency is reduced and thus engine power-output and operating-economy indicators are degraded. One of the reasons for the loss in engine efficiency is the decrease in the charge coefficient, associated with heating of the charge by the deposit layer.

Deposit formation in a combustion chamber causes a rise in the required octane number of the fuel and when the octane number of the fuel remains unchanged, deposit formation in the combustion chamber leads to an engine operating with knock or with abrupt loss in power at later ignition advance.

When an engine is being run, with increasing carbon deposits in the combustion chamber or favorable conditions are produced for knocking and the gasoline selected in advance with a specific knock resistance for this engine will become unsuitable (Fig. 111).

Studies show that the difference in antiknock properties for a new engine and for an engine that has been operated for a long time can be as much as 10-15 octane points and higher.

When an automotive engine is operated, deposits form unevenly with time. Most of the deposits are produced at the outset of vehicle operation. It was found experimentally that after a vehicle has travelled 10,000-16,000 km, a certain equilibrium state is attained and with further operation of the engine the amount of deposits varies only slightly. The equilibrium is attained because the chemical reactions and the thermal exposure together with gas currents cause combustion and removal of deposits from the combustion chamber at roughly the same rate at which they are formed at a given time. This phenomenon is known as self-cleaning of the combustion chamber. The self-cleaning process of combustion chambers was observed experimentally through a quartz window in a cylinder head. Oxidation of the gummy portion of the carbon deposits was accompanied by bright glowing.

The causes responsible for the increase in the required octane number of fuel due to carbon deposits forming in the combustion chamber of an engine can be divided into three main groups:

1. The effect of deposits on the volume of the combustion chamber. Deposits occupy some of the combustion chamber volume, and therefore the compression ratio is increased and thus the requirements imposed on the knock resistance of gasoline used rise.

2. Thermal effect of deposits. The tendency of an air-fuel mixture to knock increases with temperature. Carbon deposits exhibit good heat-insulating properties and prevent heat transfer from the hot gases to the cooling fluid. Moreover, it was found experimentally that deposits have greater heat capacity and, on absorbing heat in the combustion of fuel, release it to the new arriving portions of the mixture, by heating them to high temperatures. This combined action, the transfer of heat to fresh mixture portions and the decrease in the removal of heat from the combustion products, leads to a general rise in the temperature in the combustion chamber and promotes reactions preceding knocking.

3. Catalytic effect of deposits. Hot deposits on combustion chamber walls promote catalytic reactions causing knocking.

Effect of each of these properties of deposits on increasing the requirements on gasoline octane number differs. Numerous studies showed that the thermal action of deposits has the greatest effect.

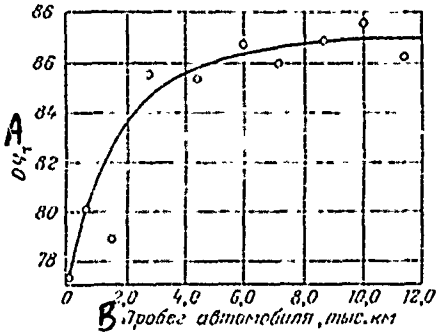

Fig. 111. Effect of vehicle run on ON_f

Key: A -- ON_f

B -- Vehicle run, 1000's km

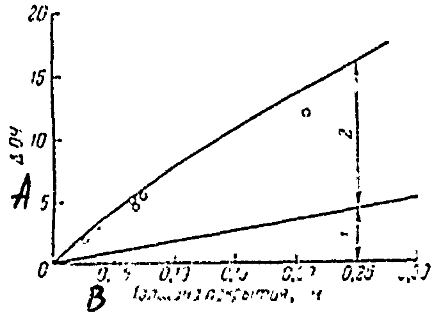

Fig. 112. Increase in required octane number when a plastic film is used:

1 -- effect due to increasing the compression ratio (found by calculation)

2 -- effect of heating insulating properties of the film

Key: A -- ON

B -- Film thickness, mm

In an experiment with a single-cylinder engine, the combustion chamber walls were coated with a thin layer of plastic (polytetrafluoroethylene [Teflon]). This material has very low thermal conductivity, does not decompose in combustion chamber conditions, and has no catalytic effect on the reactions underway. The test results showed that the increase in the required octane number is nearly proportional to film thickness. For a plastic film thickness of only 0.15 mm it is required to raise the octane number by 10 points. The increase in the engine compression ratio and the consequent rise in the requirements on gasoline knock resistance were calculated based on the thickness of the plastic film (the straight line in Fig. 112). Of the total increment in the required octane number, only 25 percent was due to the volumetric effect of the film, and the remaining 75 percent was the result of the heat-insulating action of the plastic.

The relative effect of various factors depends also on gasoline composition. When ethyl gasolines are burned, more deposits are formed but their composition contains many lead decomposition products which increase thermal conductivity (in kcal/(m·hr·deg)):

Carbon deposits for operation on ethyl gasoline	0.328
Carbon deposits for operation on nonethyl gasoline	0.205
Asbestos	0.201

Thus, when ethyl gasolines are used the relative role of the volumetric effect of deposits is greater than the effect of its heat-insulating properties on raising the knock resistance requirements of the gasolines employed.

The catalytic effect of deposits on raising the required octane number evidentally is small when either ethyl or nonethyl gasolines are used.

Earlier it was noted that carbon deposits can cause uncontrolled ignition of the working mixture. Particles of carbon deposits "glowing" in the combustion chamber can serve as a cause of the spontaneous ignition of the working mixture, which leads to engine power loss, increase in load, and noise.

Carbon deposits falling on the electrodes and insulators of the spark plugs disturbs the normal functioning of the spark plugs. This is observed especially clearly if gasolines containing organometallic antiknocks are used, since here the deposits have increased electroconductivity. In particular, one of the most essential disadvantages of the new manganese antiknock is the disruption of spark plug performance.

All the above noted disruptions in normal engine operation caused by deposit formation have taken on especially vital importance in the last 10-15 years. New uprated engines with high compression ratios are especially sensitive to deposit formation in combustion chambers. With increase in compression ratio, at the end of the compression stroke the working mixture is increasingly "prepared" for ignition; it is easily ignited by hot deposit particles. Moreover, formation of deposits in engines with high compression ratios leads to the necessity of increasing the knock resistance of high-octane gasolines, associated not only with technical difficulties, but also with large economic outlays.

Thus, the problem of reducing deposit formation in modern automotive engines with high compression ratios is paramount.

We know that not only do gasoline properties, but also the quality of the oil used affect the formation of deposits in combustion chambers [1]. Whereas the effect of oils on deposit formation has been studied to some extent and basic investigations on this problem have been published in the literature, the role of gasolines in deposit formation has been dealt with only in a few publications, sometimes containing contradictory results [2-14].

Tendency of commercial gasolines to deposit formation. Extensive work on modern automotive gasolines and their components has been conducted in recent years using a rapid method of rating deposit-forming properties of fuels and oils on an automotive carburetor engine, developed by K. K. [illegible] ... and the evaluation of test results are made based on the change in the mass of special deposit-formers inserted into the combustion chambers during the test period. The precision of the method and the reducibility of the results are quite satisfactory. The PL method yields an accelerated evaluation of gasoline tendency to deposit formation coinciding with the actual behavior of fuels in conditions of service.

The tendency of deposit formation (in mg/hr) was investigated by the PL method for a series of automotive gasolines and their components [15, 16]; here are the data for various gasolines:

Straight-run gasoline	
sample 1	5
sample 2	7
sample 3	13
Thermal cracking gasoline	
sample 1	49
sample 2	48
Catalytic cracking gasoline	17
Usual-regime catalytic reforming gasoline	
sample 1	21
sample 2	28
Drastic-regime catalytic reforming gasoline	42
A-66 gasoline	
sample 1	25
sample 2	21
sample 3	26
A-72 gasoline	13
A-76 gasoline	16
B-70 gasoline	9

The greatest tendency to deposit formation was exhibited by A-66 gasoline samples, besides thermal cracking gasolines, in the fuels investigated. The A-66 samples contain 70 percent thermal cracking gasoline and 30 percent straight-run gasoline. The minimum deposit forming tendency was observed for B-70 and A-72 gasolines. A-72 gasoline includes 70 percent catalytic cracking gasoline and about 30 percent straight-run gasoline. It must be noted that the amount of unsaturated hydrocarbons contained in A-72 gasoline was approximately the same as in A-66 gasolines.

When an automotive engine was run on B-70 aviation gasoline, deposits formed roughly 2.5-3.0 times less than for A-66 automotive gasoline.

[illegible] ... for operation on these gasolines forms only from 5 to 13 mg carbon deposits per hour. The greatest tendency to deposit formation is exhibited by thermal cracking gasoline and drastic-regime catalytic reforming gasoline. In their combustion six-to-seven times more carbon deposits are formed than in the combustion of straight-run gasolines. Gasolines of other catalytic processes are intermediate in deposit-forming tendency between straight-run and thermal cracking gasolines.

The tendency of gasoline blends to form deposits (in mg/hr), as shown by investigations, varies by the law of additivity:

	Experimental data	Calculated data
Straight-run gasoline	7.0	--
Blend of straight-run and thermal cracking gasolines, percent		
80 + 20	15.0	15.4
60 + 40	22.0	23.3
40 + 60	30.0	32.2
20 + 80	40.0	40.6
Thermal cracking gasoline	49.0	--
Catalytic cracking gasoline	17.0	--
Blend of catalytic cracking and straight-run gasolines, percent		
70 + 30	13.0	14.0
35 + 65	10.0	10.5
Blend of catalytic and thermal cracking gasolines, percent		
75 + 25	25.0	25.0
50 + 50	32.0	33.0
25 + 75	40.0	41.0
Blend of straight-run, thermal cracking, and catalytic cracking gasolines	21.0	24.3

Here, along with the experimental results are presented calculated data based on the law of additivity for this property. Clearly, deviations from the law cannot exceed the limits of precision for the method of investigation (Fig. 113). Data on the deposit-forming tendency of individual gasoline components and the additivity of this property for gasoline blends make it possible to correctly and validly approach the solution of problems of optimal component composition not only for existing , but also for new, prospective grades of commercial automotive gasolines.

When TEL is added, the deposit-forming tendency of gasolines rises sharply.

Effect of hydrocarbon composition. The hydrocarbon composition of gasoline is one of the main factors governing their tendency to form deposits in the engine. Analysis of available data shows that the tendency of automotive gasolines to form deposits can depend primarily on their content of unsaturated and aromatic hydrocarbons.

Experiments with blends of A-66 gasoline and toluene or alkylbenzene showed that adding even 30-50 percent toluene to A-66 gasoline has practically no effect on its deposit-forming tendency. Adding alkylbenzene also has no significant effect on the deposit-forming properties of A-66 gasoline. Only when 50 percent alkylbenzene was added was there some increased noted in the tendency of the fuel to form deposits. These data are given below:

	Deposits formation mg/hr
A-66 gasoline	25.0
A-66 gasoline + 30 percent toluene	26.7
A-66 gasoline + 50 percent toluene	26.5
A-66 gasoline + 30 percent alkylbenzene	27.7
A-66 gasoline + 50 percent alkylbenzene	32.0

The data suggest a conclusion that the content of unsaturated hydrocarbons in gasolines, from the standpoint of deposit formation, is more significant than in the content of aromatics. In the presence of large amounts of unsaturated hydrocarbons, aromatic hydrocarbons have virtually no effect on the deposit-forming process. However, when unsaturated hydrocarbons are absent, adding aromatic hydrocarbons to gasoline, as to be expected, increases deposit formation (Fig. 114). The addition of 30 percent toluene to B-70 gasoline increases deposit formation by nearly twofold.

The dominant role of unsaturated hydrocarbons in deposit formation can be judged by comparing the deposit-forming tendency of the gasolines B-70 and A-66. A-66 gasoline contained 16 percent unsaturated and 1 percent

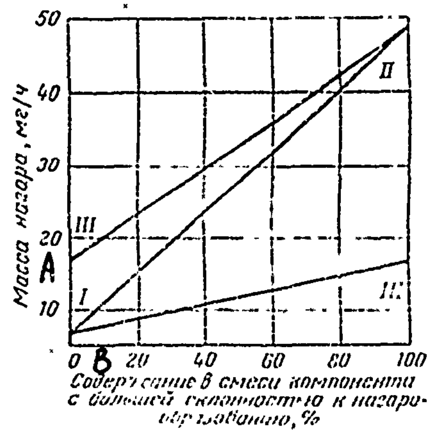

Fig. 113. Tendency of gasoline mixtures to form deposits:
1 -- straight-run gasoline
2 -- thermal cracking gasoline
3 -- catalytic cracking gasoline
Key: A -- Deposits, mg/hr
B -- Content in mixture of component with greatest deposit-formation tendency

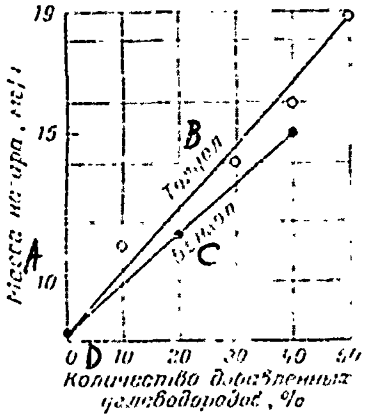

Fig. 114. Change in deposit-forming tendency of B-70 gasoline when aromatic hydrocarbons are added to it
Key: A -- Deposits, mg/hr
B -- Toluene
C -- Benzene
D -- Amount of hydrocarbons added

aromatic hydrocarbons; there were no unsaturated hydrocarbons in the B-70 gasoline, and their aromatic content was 17 percent. For operation on B-70 gasoline, 2.5-3.0 times less deposits were formed than on A-66 gasoline.

However, the total amount of unsaturated hydrocarbons in gasoline cannot serve as a criterion for rating its deposit-forming tendency. For example, A-72 gasoline contained just as much unsaturated hydrocarbon as A-66 gasoline, but the deposit-forming tendency of the former was much lower. The explanation of this fact is the different structure of the unsaturated hydrocarbons. Thermal cracking gasoline has more reactive unsaturated hydrocarbons than catalytic cracking gasoline.

The structure of unsaturated hydrocarbons, their chemical activity, and the tendency to undergo transformations at elevated temperatures is significantly accounts for the deposit-forming tendency of automotive gasolines. However, modern high-octane gasolines either did not contain any unsaturated hydrocarbons at all or else contain a small amount of relatively inactive hydrocarbons of this class. The deposit-forming tendency of such gasolines is due to the amount and structure of the aromatic hydrocarbons.

A study of the effect aromatic hydrocarbons have on deposit formation was made by the rapid PL method and also in extended tests [17]. Blends of straight-run gasoline with individual aromatic hydrocarbons of various structures and with drastic-regime catalytic reforming gasoline containing 69 percent aromatic hydrocarbons were investigated; the results of these experiments are presented below:

	Content of aromatic hydrocarbons, percent	Deposit formation, mg/hr
Straight-run gasoline	8.0	13.6
Catalytic-reforming (drastic regime) gasoline	66.0	42.0
Blend of straight-run and catalytic reforming gasolines	18.5	18.2
As above	33.0	22.7
As above	50.0	30.6
As above	66.0	41.6
Blend of straight-run gasoline with benzene	18.5	13.1
As above	46.0	11.5
As above	60.0	13.6
Blend of straight-run gasoline with toluene	19.3	16.1
As above	53.0	25.9
As above	66.0	26.1
Blend of straight-run gasoline with sec-butylbenzene	19.8	13.9
Blend of straight-run gasoline with isopropylbenzene	50.8	15.0
Straight-run gasoline with alkylbenzene fractions indicated, ° C		
114-175	21.0	17.8
114-175	47.8	16.8
114-175	57.5	20.8
114-211	12.5	16.3
114-211	31.5	18.6
114-211	50.5	28.0
Blend of straight-run gasoline with p-xylene	49.0	37.6

The structure of aromatic hydrocarbons strongly affects deposit formation. With increase in molecular weight of a hydrocarbon and in its boiling point, the effect on deposit formation as a rule becomes greater. It must be assumed that during the formation of deposits in a carburetor engine, the volatility of the hydrocarbons takes on decisive significance. Low-boiling aromatic hydrocarbons (benzene and toluene) evidentally are able to evaporate in the engine intake system, and in the preflame stages, being in the vapor phase, undergo practically no preliminary oxidation, condensation, and thickening with the formation of carbonaceous products comprising the deposits. High-boiling aromatic hydrocarbons, on remaining in the liquid phase for long time, undergo oxidative transformations on exposure to high temperatures and evidentally serve as a source of deposit formation.

Tests on the engine of the Moskvich-408 also showed [17] that as the amount of aromatic hydrocarbons is increased, the tendency of gasolines to form deposits rise both in the pure form as well as in the presence of TEL.

The results of tests (in different regimes) made of two gasolines differing widely in their content of aromatic hydrocarbons but with identical octane numbers are of interest. An engine was run in three stages of 30 hours each with a load of 25, 50, and 100 percent of the maximum at a constant rpm (2500 rpm). After the first test stage, the cylinder block head was removed, and deposits from the parts (piston head and combustion chamber) of the first cylinder were cleaned out and weighed. After the next 30 hours of operation deposits were collected and weighed from the parts of the second cylinder, and at the end of the tests -- from the parts of the third cylinder (Fig. 115).

We know that most of the deposits in a combustion chamber accumulates when an engine is run at low loads; with increase in load and with rise in the engine temperature regime, the opposite process begins -- burning out of the deposits. This process becomes especially intense in near-full throttle regimes.

Tests made (Fig. 115) showed that a content of considerable amounts of aromatic hydrocarbons in a gasoline not only increases its tendency to form deposits in the engine, but also increases the ability of the deposits to adhere firmly to the surfaces of the combustion chamber parts [17]. Thus, for example, when an engine is run on a gasoline not containing aromatic hydrocarbons in the full-load regime about 70 percent of the deposits accumulated in regime 1 are burned off, but when run on a gasoline containing 69 percent aromatic hydrocarbons, only about 20 percent of the deposits are burned off (Fig. 115).

Aromatic hydrocarbons are valuable components of automotive gasoline since they have high knock resistance. However, their content in commercial gasolines must be eliminated due to not increased deposit formation in engines. A direct comparison of the knock resistance of gasolines and their tendency to form deposits as a function of the content of aromatic hydrocarbons (Fig. 116) suggested a norm for the aromatic hydrocarbon content in commercial automotive gasolines [17].

It was found that the specific increment in the amount of deposits in a combustion chamber, that is, the increment in the amount of deposits

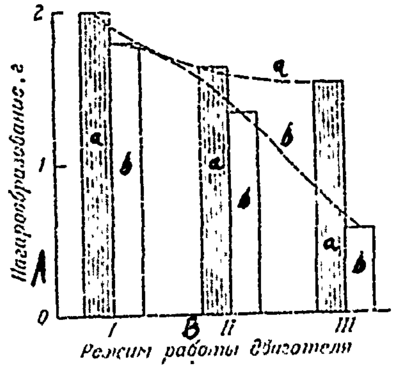

Fig. 115. Change in amount of deposits in combustion chamber of Moskvich-408 engine as a function of engine operating conditions and content of aromatic hydrocarbons in gasoline:
a -- gasoline contains 69 percent aromatic hydrocarbons
b -- gasoline contains no aromatic hydrocarbons
Key: A -- Deposit formation, g
G -- Engine operating regime

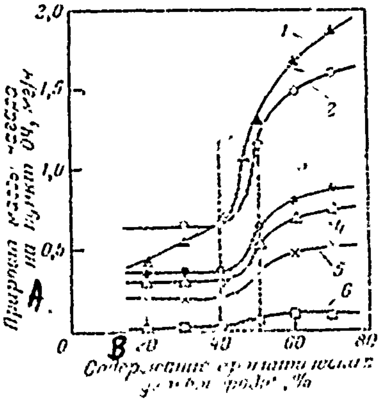

Fig. 116. Dependence of specific deposit formation on gasoline content of aromatic hydrocarbons:
1 -- straight-run gasoline from the Moscow Refinery + gasoline from the Krasnodar Refinery
2 -- as above + p-xylene
3 -- as above + butylbenzene
4 -- as above + toluene
5 -- as above + ethylbenzene
6 -- as above + benzene
Key: A -- Increment in carbon deposits per ON point, mg/hr
B -- Content of aromatic hydrocarbons

resulting from adding aromatic hydrocarbons in an amount corresponding to a 1 octane point to rise in the fuel knock resistance remains practically unchanged for various aromatic hydrocarbons when their gasoline content varies within the limits from 0 percent to 40-45 percent. For a greater aromatic hydrocarbon content, the specific increment of the amount of deposits increases sharply (Fig. 116). Thus, the content of aromatic hydrocarbons in commercial automotive gasolines must not be more than 40 percent. This norm is in need of further substantiation and verification under operating conditions.

Role of nonhydrocarbon impurities. Among the nonhydrocarbon impurities, sulfur and oxygen compounds can have the greatest effect on deposit formation. The participation of sulfur compounds in deposit formation is indicated by the fact that a relatively high sulfur content is always noted in the composition of deposits. Direct tests of gasoline containing different amounts of sulfur showed [6] that as the sulfur content in the gasoline is increased, the gasoline's deposit-forming tendency rises:

Sulfur deposit in gasoline, percent	Weight of deposits, g
0.046	1.90
0.100	2.93
0.200	4.26
0.357	5.67

The effect of oxygen-containing compounds constituting most of the resinous [gummy] compounds in gasoline on deposit formation in engines has been little studied and the data in the literature are contradictory.

A paper by N. A. Ragodin [5] summing up experience in the operation of aircraft engines noted that the use of thermal cracking gasoline with existent gum content up to 60 mg/100 ml does not lead to increased deposit formation. N. V. Brushantsev [18] noted that an increased gum content in gasolines is associated with greater deposit formation in automotive gasolines.

Investigation of a deposit-forming tendency of gasolines after different storage times, for gasolines containing different amounts of existent gums (Table 83)sshowed that a rise in the existent gum content in gasolines only slightly affects deposit formation in an engine. Gasolines differing in hydrocarbon content but with the same amount of existent gums can differ widely in deposit-forming tendencies. Thus, when thermal cracking and catalytic cracking gasolines with the same existent gum content are burned (7 mg/100 ml), 48.5 and 13.0 mg/hr of deposits are formed, respectively.

Nor was any direct relationship between deposit formation and existent gum content noted for the same gasoline. Thus, when the existent gum content in catalytic cracking gasoline was varied within the limits 7 to 17 mg/100 ml, deposit formation increased only slightly -- from 13 to 17.5 mg/hr. With a further rise in the gum content to 33 and 200 mg/100 ml, in rows, respectively, to 32 and 40 mg/hr (Table 83).

An increase in the amount of existent gums in thermal cracking gasolines (Table 84) had practically no effect on their deposit-forming tendency.

Besides these experiments, others were conducted with blends of thermal cracking gasoline similar to the same gasoline that had been "aged" in advance by storage in a thermostat at 50° C. The prepared blends corresponded in existent gum content to virtually all gasolines that are encountered in vehicular operation. A variation in the existent gum content in thermal cracking gasoline in the range 5 to 60 mg/100 ml had practically no effect on deposit formation in the engine combustion chamber:

Table 83. Change in content of existent gums and gasoline tendency to deposit formation upon prolonged storage

1 Образец	2 Условия хранения	3 Срок хранения, месяцы	4 Содержание фактических смол, мг/100 мл	5 Нагарообразование, мг/ч
Бензин термического крекинга 6	Бочка на открытой площадке 9	0	7,0	48,5
		12	26,8	52,0
		25	42,8	52,8
Бензин каталитического крекинга 7	Топливные баки автомобилей 10	0	4,0	13,0
		9	7,0	13,0
		14,5	17,0	17,4
		20	11,0 *	17,4
		29	32,0 *	32,5
		29	200,0	40,0
Бензин прямой перегонки 8	Бочка на открытой площадке 11	0	3,0	6,8
		12	3,0	7,0
		25	4,0	7,0

* Part of the gums precipitated to the tank bottom.

Key: 1 -- Sample
2 -- Storage conditions
3 -- Storage time, month
4 -- Content of existent gums, mg/100 ml
5 -- Deposit formation, mg/hr
6 -- Thermal cracking gasoline
7 -- Catalytic cracking gasoline
8 -- Straight-run gasoline
9 -- Drum in open area
10 -- Vehicle fuel tanks
11 -- Drum in open area

Existent gum content, mg/100 ml	Deposit formation, mg/hr
5	48
23	51
60	49

Similar results were obtained after gummy compounds were removed from thermal cracking gasoline by filtration through a layer of active aluminum oxide. As a result, the hydrocarbon portion of the gasoline remained practically unchanged, while the gummy substance content (adsorptive gums) was significantly reduced. Tests of the initial thermal cracking gasoline and the same gasoline after being filtered through the aluminum oxide showed that even the total gummy substance content in the gasoline had

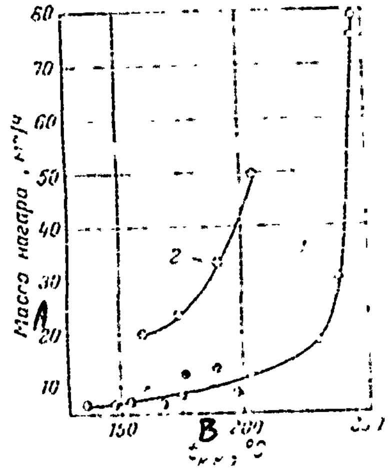

Fig. 117. Dependence of gasoline tendency to form deposits on gasoline end boiling point:
1 -- straight-run gasoline
2 -- thermal cracking gasoline
Key: A -- Deposits, mg/hr
B -- $t_{e.b}$

practically no effect on engine deposit formation. These data afford the confident statement that existent gum content in gasoline is practically without effect on deposit formation in an engine. However, when an engine is run for long periods on gasolines with high existent gum content or even for short tests on gasolines with extremely high content of these gums, a slight rise in deposit formation was noted, a consequence of of the mechanical removal of some of the gummy deposits from the intake system into the combustion chamber.

Effect of fractional composition. When examining the question as to the effect that the structure of aromatic hydrocarbons has on their tendency to form deposits, we referred to their volatility values. High-boiling aromatic hydrocarbons have a stronger effect on deposit formation than low-boiling aromatic hydrocarbons. In other words, deposit formation in an automotive engine obviously is directly associated with the fractional composition of the gasolines used. Also in favor of this hypothesis are the observations published in the literature stating that when vehicles are operated on "lighter" gasolines the octane number requirements (equivalent to deposit-forming intensity) are increased to a lesser extent than for "heavier" gasolines [2, 3, 19]. From the literature we also know that lightening the fractional composition of diesel [20, 21] and jet [22] fuels leads to a reduction in deposit formation in an engine.

To find the effect that the fractional composition of gasolines has on their deposit-forming tendency, thermal cracking and straight-run gasolines with different end boiling points were tested. In thermal cracking gasolines, the deposit-forming tendency rises quite sharply with an increase in the end boiling point from 175 to 190 and 205° C. For straight-run gasolines, the deposit-forming tendency increases only very slightly when the end boiling point is raised within the limits from 150 to 220-225° C (Fig. 117). Only a further rise in the end boiling point to 247° C leads to a sharp increase in deposit formation. It must be noted that all blends of gasolines and initial fuels studied contain roughly the same amount of aromatic hydrocarbons (from 13 to 17 percent) and gummy compounds (to be existent gum content was in the range 2 to 4 mg/100 ml).

An appreciable reduction in deposit-forming tendency of commercial automotive gasolines can be achieved by lowering the end boiling point of the thermal cracking component to 170-180° C.

Deposit-forming mechanism. Most of the gasoline is completely evaporated in the engine intake manifold. In the vapor state gasoline hydrocarbons are not subject to chemical transformations during the preflame period and burn without forming large amounts of deposits. Some of the gasoline is unable to evaporate in the intake manifold and enters the combustion chambers in the form of droplets, sometimes as a mist. Being in the liquid phase, high-boiling hydrocarbons can undergo chemical changes under the effect of the temperature in the preflame stages. These changes, associated with oxidation of a hydrocarbon and its subsequent condensation, polymerization, and the thickening of oxidation products, lead to high-molecular products subsequently forming deposits. The tendency of a gasoline to form deposits is determined by the chemical stability of high-boiling fractions. If these fractions are stable, then their quantity only slightly affects deposit formation; if unstable, their content fully determines the deposit-forming properties of the gasolines.

To confirm the above concepts, in addition to the earlier-described experiments, a study was made of the deposit-forming tendency of various thermal cracking gasoline fractions. The experiments showed that adding light fractions of thermal cracking gasoline to straight-run gasoline has practically no effect on the amount of deposits formed. High-boiling fractions of thermal cracking gasoline, whose composition includes about 30 percent extremely unstable unsaturated hydrocarbons, caused a sharp rise in the deposit-forming properties of straight-run gasoline (Fig. 118). Decreased acceleration in deposit formation was caused by adding the 190-205° C fraction, and the least -- by adding the 160-205° C fraction (Fig. 118). These data fully confirm the views presented above.

Since the deposit-forming tendency of gasolines depends on the thermal stability of high-boiling fractions, then by estimating this stability in laboratory conditions one could predict the deposit-forming properties of gasolines.

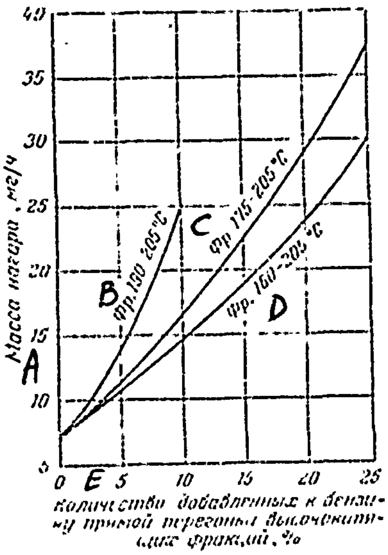

Fig. 118. Effect of high-boiling fractions of thermal cracking gasoline on the deposit-forming tendency of straight-run gasoline

Key: A -- Deposits, mg/hr
B -- 190-205° C fraction
C -- 175-205° C fraction
D -- 160-205° C fraction
E -- Amount of high-boiling fractions added to straight-run gasoline

A standard LSART instrument can be used to find the thermal stability of automotive gasolines. The stability is estimated by oxidizing 25 ml gasoline in hermetically sealed small bombs in the presence of copper strips at 165° C, for 1 hour. At this temperature some of the gasoline is in the vapor stage and undergoes oxidation, principally the high-boiling gasoline fractions. The total amount of gummy substances (potential gums) formed in the gasoline during the oxidation time is the criterion of stability.

These results (Fig. 119) showed that estimating the thermal stability of gasoline in selected conditions corresponds to its deposit-forming tendency in combustion chambers. As the amount of potential gums in a

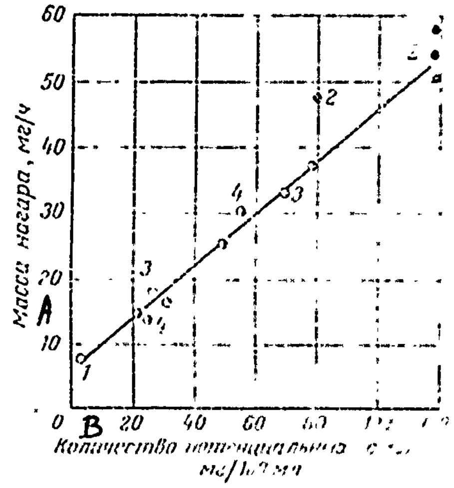

Fig. 119. Effect of amount of potential gums in gasolines and on their deposit-forming tendency:

1 -- straight-run gasoline
2 -- thermal cracking gasoline
3 -- catalytic cracking gasoline
4 -- blends of straight-run gasoline with end fractions of thermal cracking gasoline

Key: A -- Deposits, mg/hr
B -- Amount of potential gums, mg/100 ml

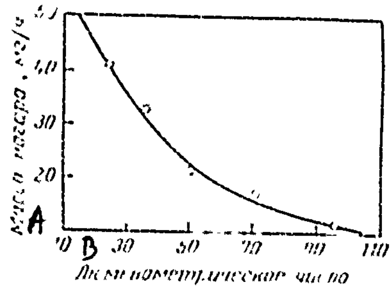

Fig. 120. Relationship of luminometric number of fuels and their deposit-forming tendency

Key: A -- Deposits, mg/hr
B -- Luminometric number

gasoline is increased, its deposit-forming properties deteriorate according to a law of proportionality. This regularity is valid for gasolines produced in various processes. Thus, the presence of a direct relationship between the thermal stability of high-boiling fractions of a gasoline and its tendency to form deposits makes it possible to devise a laboratory method for estimating deposit-forming properties of automotive gasolines based on their thermal stability.

Recently, abroad a parameter such as the "glow number" (luminometric number) characterizing the brightness of flame in fuel combustion is often used for a laboratory rating of the deposit-forming properties of fuels. A fuel whose combustion produces a flame containing particles of coke and carbon black burns brighter. This kind of fuel has a low luminometric number compared with fuel whose combustion flame is less bright. This method was used [17] to determine the "glow number" of gasoline samples with different aromatic hydrocarbon content. The results were compared with data on carbon deposits in combustion chambers (Fig. 120).

From the data in Fig. 120 it follows that the amount of deposits in an engine when run on gasolines with different aromatic hydrocarbon content is related in some way to their "glow numbers." As the aromatic hydrocarbon content in gasolines is increased, the "glow number" is reduced and thus the amount of deposits forming in the combustion chamber correspondingly rises. This makes it possible to use the "glow number" to rate the approximate tendency of a gasoline to form deposits in the engine.

Possibility of reducing carbon deposits. All methods of lowering deposit formation in an engine can be divided into three groups:

1. Design measures aimed at improving the combustion process -- upgrading its completeness. Substantial successes have been gained in this direction. Organizing flows in the combustion chamber, producing conditions for burning out the deposits, and several other methods are capable of reducing deposit formation. This group must be regarded as including efforts to find coatings for the surfaces of combustion chamber walls on which deposits would not form. Coatings made of copper, tin, cadmium, chromium, molybdenum, and even tin have been investigated, but thus far the desired results have not been achieved.

2. Adjustment of the chemical and fractional composition of the fuels employed. Lowering the end boiling point, restricting the content of unsaturated and aromatic hydrocarbons in gasolines, and reducing the sulfur content all goes to promote reduced deposit formation. However, these measures have not found wide practical use since they involve decreased gasoline yields and changes in gasoline operating properties.

3. Introducing additives. Searching for additives reducing the total deposit amount in an engine has not yet been concluded and additives of this type have not found practical use.

Deposits in the Intake System

In considering deposit formation in an engine it was noted that the gum content in a gasoline does not affect the amount of deposits since most of these compounds are deposited even before the gasoline enters the combustion chambers. The most favorable conditions for forming gum deposits are produced when gasoline evaporates in the engine intake manifold.

In a fully warmed engine operating in the steady-state regime, only a small part of the heavy gasoline fractions enters the walls of the intake manifold and moves along them toward the engine cylinders. Along with the heavy gasoline fractions, most of the gummy compounds in the gasoline are in the liquid film. Naturally, the concentration of gummy compounds in the liquid film is tens of times greater than the concentration of gums in the initial gasoline. Along the route from the carburetor to the intake valve the liquid film is continuously heated by the exhaust gas or by the coolant for better evaporation. In these conditions there is quite vigorous oxidation not only of the hydrocarbon part of the gasoline, but of the earlier-accumulating gums, forming products that are insoluble in gasoline. Precipitating gums are deposited on the walls of the intake manifold and the intake valve stems, where on exposure to the temperatures they are converted into hard, difficult-to-remove deposits.

A layer of gum deposits reduces the cross-section of the intake manifold and produces additional drag in the suction line. As a result, charging of engine cylinders with the combustible mixture is deteriorated. In automotive operating practice, there have been cases in which the cross-section of the intake manifold was reduced by 70-80 percent due to deposit formation [22]. Stand tests of automotive engines showed that the power and operating economy of new engines is reduced by more than 50 percent when intake manifolds taken from vehicles that have covered more than 100,000 km are installed in them [24, 25].

Deposits forming in intake manifold exhibit poor thermal conductivity, which hinders the supply of heat to the working mixture and thus deteriorates fuel vaporization conditions. Deposits of this type forming on the stems and heads of the intake valves disrupt normal operation of the valve mechanism and can lead to jamming of the valves. These effects are accompanied by reduced engine power and operating economy.

The composition and properties of deposits depend on numerous operating conditions. The organic portion of deposits is usually 70-90 percent, and the rest is inorganic, compounds precipitating in the intake manifold from the air and the gasoline. Deposits in the intake manifold contain less organic impurities than deposits in the intake valves. Generally, the composition of deposits along the route of the intake line are inconstant. The content of asphaltenes is reduced in the organic portion of deposits, with decreasing proximity to the carburetor and the content of carbenes and carboids rises. Thus, whereas the organic part of the deposits forming directly beyond the carburetor are two-thirds asphaltenes deposits on the intake valve head contain only 3-5 percent asphaltenes, while two-thirds of the deposits are carbenes and carboids.

The composition of the inorganic part of the deposit varies to a lesser extent along the length of the intake line. The content of lead compounds rises steadily and is more than one-third of the entire amount of inorganic compounds at the intake valve head. The content of the remaining constituents of the inorganic portion -- silicon oxide and ferric oxide -- varies little.

For a long time no systematic study was made of the formation of the deposits in an engine owing to the absence of a reliable method of a rapid estimate of the amount of deposits formed. The methods known in the literature are based either on long-term tests on full-size engines [25, 26], or else on the evaporation of gasoline in various laboratory instruments in a stream of air, steam, or inert gas [26-28].

Not only is a long time required for full-sized engine tests, but also a large amount of the test fuel sample, and the estimate of the results proves to be considerably hindered owing to the complex configuration of the intake manifolds. Laboratory methods provide only an approximate estimate of the tendency of gasolines to form deposits owing to the large number of conditions and assumptions that detract from their precision.

Recently a laboratory method of testing gasolines [29] was developed for a single-cylinder engine stand to determine octane numbers, permitting rapid and reliable rating of a fuel's tendency to form deposits in the engine intake manifold. The single-cylinder engine of the stand used to determine octane numbers does not require large amount of fuel, and the stand equipmentation permits varying such parameters as the temperature of the air-fuel mixture and the intake air, as well as composition of the air-fuel mixture over fairly wide limits and also permits maintaining these parameters constant during the test period.

A removable plate curved to match the shape of the intake manifold is inserted into it for a quantitative estimate of the deposits formed. The amount of deposits forming for operation on a given gasoline is estimated by the increase in the weight of the strip after the test period.

Effect of gasoline stability and gasoline content of gums. Using the above-described method, the effect of the gum content in gasoline on deposit formation in the engine was investigated. The gum content in gasoline was estimated by two techniques. The content of existent gums was determined by the standard method, additionally, the total content of gums in the gasoline was estimated by filtering the gasoline through a layer of adsorbent (aluminum oxide), followed by quantitative determination

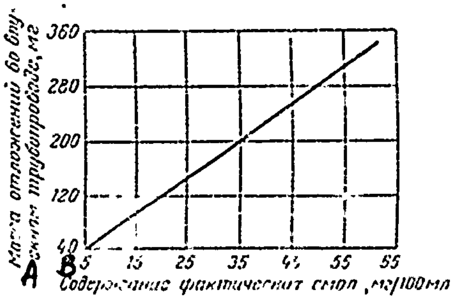

Fig. 121. Dependence of amount of deposits in engine intake system on existent gum content in gasoline
Key: A -- Deposits in intake manifold, mg
B -- Content of existent gums, mg/100 ml

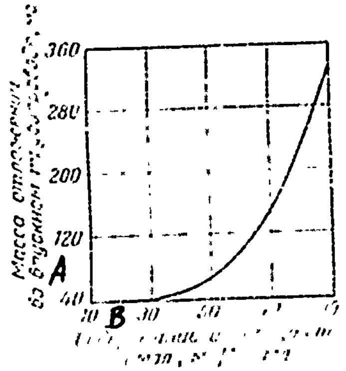

Fig. 122. Dependence of amount of deposits in engine intake system on content of adsorbed gums in gasoline
Key: A -- Deposits in intake manifold, mg
B -- Content of adsorbed gums, mg/100 ml

Table 84. Effect of combustible mixture temperature on deposit formation in engine intake system (test period -- 4 hours at $\alpha = 0.95$)

1 Температура горючей смеси, °C	2 Количество отложений во впускной [illegible] фактических смол в бензине, [illegible]			
	1,4	3,6	5,9	[illegible]
25	1,3	0,9	1,4	—
50	26,8	[illegible]	31,3	[illegible]
100	36,3	[illegible]	30,4	15,3
150	8,9	22,1	26,1	[illegible]

Key: 1 -- Combustible mixture temperature
2 -- Amount of deposits in intake system, mg, for indicated content of existent gums in gasoline, mg/100 ml

of the sum of gums desorbed from the adsorbent. The amount of these "adsorptive gums" characterizes the presence of gummy compounds which were already in the gasoline and which can participate in forming deposits in the engine intake system.

Commercial A-72 gasoline with different gum content underwent testing; the different gum contents were attained by blending the initial gasoline with various amounts of the same gasoline that had previously been "aged" by being stored in a thermostat. The results (Fig. 121) shows that there is a virtually linear relationship between the existent gum content in gasoline and the formation of deposits in the engine intake system. When the existent gum content in the gasoline is raised from 10 to 20 mg/100 ml, the amount of deposits also rises by about twofold.

The dependence of the amounts of deposits on the content of adsorptive gums shows a somewhat different trend (Fig. 122). Obviously, not all gummy compounds determined as adsorptive gums participate in forming deposits. Low-molecular oxidation products evidently can be evaporated in the intake manifold without forming deposits. And the fraction of the gums evaporating in the intake manifold depends on the temperature conditions. This principle was well confirmed by results of studies made by N. A. Ragozin (Table 84). The largest amount of deposits is formed at 50-100° C. Evidentally, at 25° C no further oxidative transformations of the preciptating gums occur and the amount of deposits is low. At 150° C most of the gums have been evaporated and the amount of the deposits formed is also small.

The conditions for deposits forming in the intake manifold are such that in addition to the precipitation of gums previously contained in the gasoline, new oxidation products also preciptating in the intake system can be formed. In other words, it can be assumed that some of the deposits are formed due to oxidation of unstable gasoline compounds directly in the intake manifold. If this is valid, gasolines with different oxidizabilities can form different amounts of deposits.

The study made showed that gasoline differing in chemical stability have different tendency to form deposits in the intake system:

	Amount of deposits on the strip, mg	Induction period, min
A-66	22	340
A-72	10	1000
B-70	6	1000
Straight-run gasoline	4	1000
Thermal cracking gasoline	43	110
Catalytic cracking gasoline	19	885

All the gasolines tested contain approximately the same amount of initial gum content (2-4 mg/100 ml). A-66 gasoline contained about 50 percent thermal cracking gasoline, and A-72 gasoline -- 70 percent single-stage catalytic cracking gasoline. Among the components investigated, the greatest tendency to oxidation and deposit formation was shown by thermal cracking gasoline, and the least -- by straight-run gasoline.

These data show that there is a definite relationship between the oxidizability of a gasoline and its tendency to form deposits. The longer the induction period of the oxidation of a gasoline, the less deposits are formed in the intake system after the gasoline has evaporated.

N. A. Ragozin, who studied the effect of the unsaturated hydrocarbon content in aviation gasolines on deposit formation in the intake system, reached a similar conclusion:

Unsaturated hydrocarbon content in gasoline, percent	Iodine number, mg I_2/100 g gasoline	Amount of deposits in the intake manifold, mg
4.0	10	31.3
3.5	9	26.8
2.0	5	19.7
0.7	2	1.7

As the unsaturated hydrocarbon content is increased, that is, the material that can be oxidized in the intake system, the tendency of a gasoline to form deposits rises.

We know that the induction period of gasoline oxidation can be significantly increased by adding anti-oxidants. It was of interest to verify whether anti-oxidants retard oxidation in the intake manifold and thus reduce the formation of deposits.

The most common and best-tested anti-oxidants were investigated: lignoresin, phenols of coal origin, and p-hydroxydiphenylamine. Results showed that anti-oxidants have only a very slight effect on deposit formation:

	Deposit content on strip, mg	Induction period, min
A-66 without oxidant [sic]	22	340
As above, containing 0.01 percent p-hydroxydiphenylamine	17	600
As above, containing 0.1 percent FCh-16 anti-oxidant	18	900
As above, containing 0.1 percent lignoresin anti-oxidant	28	480

p-Hydroxydiphenylamine and coal-origin phenols somewhat reduce the amount of deposits formed, while lignoresin anti-oxidant even somewhat increases the deposits.

Anti-oxidants are intended to prevent the oxidation of unstable gasoline compounds at ordinary presence in storage conditions. Oxidizing processes in the intake manifold at elevated temperatures and with the high oxidation service of the gasoline are inhibited by an anti-oxidant to a lesser extent. Lignoresin anti-oxidant contains some amount of high-boiling compounds of the neutral oil type which are incompletely evaporated in the intake manifold and on exposure to high temperatures undergo changes, forming solid deposits. Thus, the induction period of oxidation to some extent characterizes oxidizability in the intake system only for gasolines not containing anti-oxidants.

Evidentally, only those high-boiling compounds that remain in the liquid phase for some time are subject to oxidation in the intake manifolds. In other words, the thermal stability of high-boiling gasoline fractions must to some extent determine the tendency of the gasoline to be oxidized in the intake system.

To verify this hypothesis, the thermal stabilities of several gasolines and components were rated in the LSART instrument at 165° C in the presence of copper strips. The rating method adopted was the same as that used in studying the tendency of gasolines to form deposits. The results indicate that there is a relationship between the thermal stability of a gasoline as its tendency to form deposits:

	Potential gum content after oxidation of gasoline at 165° C, mg/100 ml	Amount of deposits on strip, mg
A-72	32	12
A-66	95	28
B-70	3	5
Straight-run gasoline	2	3
Thermal cracking gasoline	120	45
Catalytic cracking gasoline	70	18

This function is not linear (as in the case of deposit formation), although the amount of deposits formed also increases with higher potential gum content in a gasoline.

It must be assumed that a gasoline's tendency to form deposits in the intake system is associated with oxidation of high-boiling fractions present as a liquid film on the intake manifold walls. The oxidation of individual gasoline droplets suspended in the stream of the air-fuel mixture evidentally determines deposit formation in engine combustion chambers. Thus, the tendency of gasoline to form deposits in the intake system of an engine depends on the gasoline's gum content and to the thermal stability of its highest boiling fractions, while the tendency of a gasoline to form deposits is determined only by the thermal stability of the high-boiling fractions.

Several new problems. Over the last 8-10 years measures have been begun to control atmospheric pollution from the operation of automotive engines. One measure is the installation of a system of forced crankcase ventilation aimed at sucking the crankcase gases into the engine's intake system. Crankcase gases contain products of incomplete gasoline combustion, highly minute droplets of oil, water vapor, and so on. On entering the intake system they contaminate the venturi and the throttle and increase the amount of deposits in the intake manifold [30]. Contamination of the throttle is observed in any conditions of use, but is specially severely during the hot time of the year. Contamination is intensified when a vehicle travels in the low-temperature regime -- urban or city travel with frequent stops. In this case the amount of condensation products entering the intake system is increased.

Adding special additive exhibiting "detergent" properties of a gasoline proved to be the most effective way of controlling carburetor contamination. Automotive gasolines containing detergent additive appeared in the United States in 1964 [31]. Tests showed that the disruption in normal carburetor operation due to carburetor contamination can occur in 13,000 km during the summer and in 15,000 km during the winter. Adding a detergent additive to the gasoline in the same conditions permits extending the operating time of an engine without malfunctioning to 32,000 km. It was found that adding detergent additives to gasoline reduces the amount of deposits also in the intake manifolds.

At present, the following detergent additives are produced and used abroad: Enjay Paradyne 44, Amco 572, Monsanto Santolene L, and Lubrisol 580. These additives are used in gasoline in the amount of 0.001-0.01 percent [32].

It must be noted that the use of detergent additives is economically justified, since it only slightly adds to the cost of the gasoline [32].

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[To Chapter Seven]

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CHAPTER EIGHT
CORROSIVENESS OF GASOLINES

Automotive gasolines come in contact with the most diverse metals in transportation, storage, and use. When exposed to fuel the steel in pipelines and reservoirs, copper, brass, and other alloys of the automotive fuel system undergo corrosive attack. At the present time it has been established that hydrocarbons present in gasolines have no corrosive effects on metals and alloys. The corrosiveness of gasolines is due to their content of nonhydrocarbon impurities, and primarily sulfur and oxygen compounds and water-soluble acids and alkalis.

The corrosiveness of automotive gasoline is a little-studied field of fuel use, even though the study of the corrosive properties of gasolines began more than 40 years ago. Evidentally, two factors serve as an impetus for research on the corrosive properties of gasolines: first of all, experience in the composition of commercial automotive gasolines of the products resulted from thermal processes in the secondary refining of crudes whose hydrocarbons are prone to be oxidized, forming acidic products; and secondarily, the inclusion in refining stocks of sulfur crudes, which led to a rise in the sulfur compound content in commercial gasolines.

Water-soluble acids and alkalis as a rule are random gasoline impurities. Of this group of corrosive agents, alkali can be present more often than others. Based on the current technology for producing automotive gasoline components, they are all washed with an 8-12 percent alkali solution. Next, the gasolines are scrubbed with water. When a gasoline is inadequately scrubbed, the alkali wash can leave traces of alkali.

The presence of traces of sulfuric acid or its acid esters in domestic gasolines is virtually excluded since the sulfuric-acid purification of gasoline distillates is not used at all refineries. Water-soluble acids can include sulfo-acids formed in the profound oxidation of certain organic sulfur compounds.

Other water-soluble acids and alkalis can enter a gasoline when dirty containers, pipelines, and so on are used.

Water-soluble acids cause intense corrosion in any metals, while alkalis corrode aluminum, therefore their presence in automotive gasolines is unacceptable. Water-soluble acids and alkalis are determined by a qualitative test in GOST 6307-60. The gasoline is agitated with an equal amount of water in a separatory funnel, and the pH of the aqueous extract is checked with indicators (methyl orange and phenolphthalein).

Increased corrosiveness of ethyl gasolines is due to the formation of hydrogen halide acids when halogen scavengers react with water.

Rating Methods

One of the serious barriers to the study of the corrosiveness of gasoline was the absence of rapid quantitative laboratory methods. The methods of estimating corrosiveness described in the literature are qualitative [1, 2] or too lengthy, since they involve prolonged storage of samples [3-6]. In general, laboratory storage at a specific temperature has a key fundamental disadvantage as a method of rating the corrosive properties of fuels. In these conditions there is no temperature drop and the associated condensation of moisture on the surfaces of fuel contact with the metal, which hampers the manifestation of electrochemical corrosion.

Studies by L. G. Gindin [7-9], I. A. Pgashinskiy and R. I. Guseva [10], D. I. Mirlas [11-17], and many others showed that the corrosion of metals in petroleum products in the presence of moisture is electrochemical in nature. In actual conditions of gasoline storage and use, besides electrochemical corrosion there are also purely chemical processes, but the overall corrosive effect is determined by the electrochemical process, since its rate significantly exceeds the rate of chemical corrosion by the corrosive gasoline components.

Thus, to rate the overall corrosiveness of gasolines one must first study their corrosiveness in conditions of electrochemical corrosion. Therefore the method of rating the corrosive properties of gasolines must continually reproduce conditions for the electrochemical corrosion of a metal specimen. These conditions were provided in a recently developed instrument [18, 19], and on the basis of this a technique for rating the corrosive properties of fuels and the effectiveness of anti-corrosion additives was proposed.

The instrument (Fig. 123) is a two-walled flask. The internal flask serving as a reservoir for the test fuel houses a hollow glass base 6 for the metal strip and a groove into which distilled water is poured, thereby providing maximum humidity of the enclosed air and the fuel. The groove ensures rapid evaporation of the water and prevents the possibility of test fuel vapor condensing on the water surface, since the water rapidly acquires the temperature of the liquid arriving to heat the flask. The external flask (a water jacket of the internal flask) is equipped with outlets to supply water from the thermostat.

The test method consists of the following. Fuel (60 ml) is poured into the inner flask of the instrument. A carefully cleaned and precisely weighed round metal plate, 20 mm in diameter and 4 mm thick is placed on the water-cooled glass base. The plate is provided in its center with a M3-thread opening for convenience in inserting it into the instrument. Into the instrument groove is poured distilled water (to the very edge) and water heated to 70° C in the thermostat is released between the instrument walls.

Before weighing the plates after the experiment, the corrosion products are removed from them. The corrosion products from plates made of ferrous metals are removed by etching for 5-7 minutes in a 20 percent aqueous solution of hydrochloric acid containing 0.8-1.0 percent PB-8 inhibitor [2] (the inhibitors BA-6, BA-12, and so on can also be used). Then the plates are washed for 3-5 minutes in a 5 percent calcined soda solution in a mixture of alcohol and gasoline, and are then dried and weighed. The corrosion products of the glass plates are removed mechanically; it was found that this can be done best by using an ordinary pencil eraser. The plate corrosion is expressed in g/m^2.

The reproducibility of the results of rating fuel corrosiveness by the method developed is quite satisfactory. Deviation from the mean is not more than ± 0.5 g/m^2 for corrosion not exceeding 10-15 g/m^2, and ± 1.0 g/m^2 -- for more severe corrosion.

The main accelerating factor in the method of rating gasoline corrosiveness is high humidity and constant condensation of water vapor on the metal plate. Without the water vapor, corrosion (in g/m^2) of the steel plates is much less in the test conditions:

	With water	Without water
Diisobutylene	8.2	1.8
Gasoline		
straight-run	0.4	0.0
thermal reforming	8.9	0.5
thermal cracking before storage	4.8	0.2
thermal cracking (after storage)	10.5	1.4
catalytic cracking	2.3	0.0
catalytic cracking of heavy crude	18.0	0.8

It is interesting to note that oxidation of unsaturated hydrocarbons in the absence of water vapor over the surface proceeds more intensively.

But even given the higher concentration of the concentration products, the corrosion of steel plates in the absence of a water film on the surface occurs at a much lower rate (Table 85).

The rating of gasoline corrosiveness by the accelerated method agrees fully satisfactorily with the actual corrosive properties of fuels in storage conditions (Table 86). Storage was provided in a thermostat at variable temperatures (20-40° C) and high humidity.

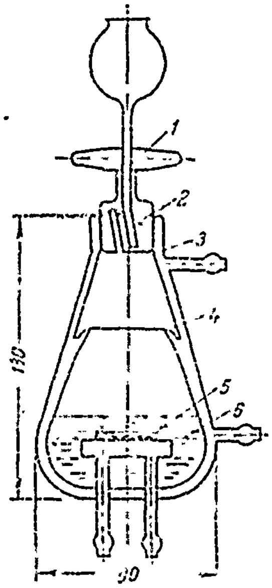


Fig. 123. Instrument for rating gasoline corrosiveness in conditions of water condensation:

1 -- plug with water trap
2 -- water trap
3 -- double-walled flask
4 -- channel-groove for water
5 -- metal plate
6 -- glass base, water-cooled

As we can see from the data in Table 86, relatively limited corrosion of steel plates upon storage (0.7-0.9 g/m^2) is observed in the presence of gasolines that exhibit corrosiveness up to 4.0-4.5 g/m^2 based on the rapid method. These gasolines show visible corrosion on steel plates only by the ninth to tenth month of storage at 40° C. Thus, when the rapid method is used gasolines showing corrosion less than 4.5 g/m^2 can be regarded as noncorrosive, while those showing a value higher than 4.5 g/m^2 can be

Table 85. Effect of water on the oxidizability and corrosiveness of diisobutylene (experiment duration 4 hours at 70° C)

Показатель 1	До испытаний 2	После испытаний с водой 3	После испытаний без воды 4
Коррозия, г/м² 5	—	8,2	1,8
Кислотность, мг KOH/100 мл 6	0,8	0,5	1,3
Перекисное число, г O_2/100 мл 7	3,3	3,3	5,1

Key: 1 -- Indicator
2 -- Before tests
3 -- after testing with water
4 -- after testing without water
5 -- corrosion, g/m²
6 -- acidity, mg KOH/100 ml
7 -- peroxide number, g O_2/100 ml

regarded as corrosive. The established criterion for rating the corrosiveness of gasolines (up to 4.5 g/m²) naturally needs further verification and refinement for a large number of samples.

The results of rating the corrosiveness (in g/m²) of gasolines of various origins by the above-described method are presented below:

Thermal cracking gasoline	4.5
Catalytic cracking gasoline	2.9
Thermal reforming gasoline	8.9
A-66 gasoline after storage, sample 1	9.5
As above, sample 2	3.5
As above, sample 3	7.0
A-72 gasoline after storage	4.6
B-70 gasoline after storage	4.1
A-72 gasoline from the column	2.0
A-66 gasoline from the column, sample 1	2.0
As above, sample 2	4.2
A-76 gasoline from the column	3.0
B-70 gasoline	2.2
Ekstra gasoline	2.2
A-76 gasoline	1.8

Table 86. Corrosiveness of gasolines rated by the rapid laboratory method (70° C, 4 hours) and rated after storage in a thermostat for 10 months

Образец 1	Коррозия стальной пластинки, г/м² 2	
	по ускоренному методу 3	при хранении в термостате 4
Бензин каталитического крекинга 5	2,9	0,7; после 10 месяцев — редкие, еле заметные очаги коррозии 15
Бензин каталитического риформинга 6	1,8	0,7; то же 16
Бензин термического крекинга 7	2,5	0,8; »
Бензин термического риформинга 8	8,9	1,65; через 2,5 месяца появилась видимая коррозия 17
Бензин прямой перегонки (сернистый) 9	5,8	1,0; через 9 месяцев появилась коррозия через 10 месяцев коррозия покрывала около $^1/_4$ пластинки 18
Бензин А-72, образец 1 10	4,5	0,9; через 9 месяцев появилась коррозия 19
» А-72, образец 2 11	9,5	1,6; через 4 месяца появилась коррозия 20
» А-66, образец 1 12	4,2	0,9; через 9 месяцев появилась коррозия 21
» А-66, образец 2 13	5,2	1,1; через 6 месяцев появилась коррозия 22 через 10 месяцев коррозия покрывала около 25% площади пластинки 23
» А-66, образец 3 14	7,0	1,5; через 6 месяцев появилась коррозия 24 через 10 месяцев 50% площади пластинки покрылась очагами коррозии 25

Key:
1 -- Sample
2 -- Corrosion of steel plate, g/cm^2
3 -- by rapid method
4 -- after storage in thermostat
5 -- Catalytic cracking gasoline
6 -- Catalytic reforming gasoline
7 -- Thermal cracking gasoline
8 -- Thermal reforming gasoline
9 -- Straight-run (sulfur crude) gasoline
10 -- A-72 gasoline, sample 1
11 -- A-72 gasoline, sample 2
12 -- A-66 gasoline, sample 1
13 -- A-66 gasoline, sample 2
14 -- A-66 gasoline, sample 3
15 -- infrequent, barely detectable centers of corrosion after 10 months
16 -- as above
17 -- visible corrosion appeared in 2.5 months
18 -- corrosion appeared in 9 months; the corrosion covered about one fourth of the plates in 10 months
19 -- corrosion appeared in 9 months
20 -- corrosion appeared in 4 months
21 -- corrosion appeared in 9 months
22 -- corrosion appeared in 6 months
23 -- in 10 months corrosion covered about 25 percent of the plate area

[Key concluded on following page]

[Key concluded for Table 86 on preceding page]:

24 -- corrosion appeared in 6 months
25 -- in 10 months 50 percent of the plate area was covered by corrosion centers

The highest corrosion of steel plates was obtained when tests were made of thermal cracking gasoline and certain commercial gasoline samples after storage.

Effect of Ogygen-containing Compounds

Oxygen-containing compounds, in contrast to water-soluble acids and alkalis, are not random impurities of gasolines but are always present to some extent. They can enter gasoline from the crude or from its distillates during refining processes and can also form in the oxidation of the most unstable gasoline hydrocarbons in gasoline storage and transporting.

Among the oxygen-containing compounds entering gasoline from crude, naphthenic acids exhibit the greatest corrosiveness. However, they have marked corrosive effect only on lead and zinc, while they have a slight effect on other nonferrous metals, and still less so on ferrous metals. Thus, after a 3-month contact of metals with a solution of unpurified naphthenic acids at room temperature, their weight loss (in g) was as follows [20]:

Lead	6.10	Antimony	0.11
Zinc	4.68	Iron	0.08
Copper	0.56	Aluminum	0.00
Tin	0.18		

Ordinarily gasolines contain very little naphthenic acids; their amount is determined by gasoline acidity. Gasoline acidity is determined according to GOST 5985-59 by extracting acids from the gasoline with boiling ethyl alcohol, followed by titration with an alcoholic solution of potassium hydroxide; it is expressed in the amount of KOH (in mg) required to neutralize 100 ml of gasoline. The acidity of straight-run gasolines and freshly produced secondary-origin gasolines usually does not exceed 0.3-0.5 mg KOH/100 ml. Commercial automotive gasolines on coming from their refinery may have an even higher acidity (up to 3 mg KOH/100 ml) due to the acidic properties of phenolic type anti-oxidants added for the chemical stabilization of gasolines. However, the corrosiveness of phenols as a rule is very low and some of them are good corrosion inhibitors. The acidity of gasolines containing phenolic compounds can be somewhat reduced upon storage as the anti-oxidant is consumed.

Most oxygen compounds are formed in gasoline when it is in storage or in transit. Acidic products of the oxidation of unstable compounds have much greater corrosiveness than acetic acids, and all the more so because some of them are soluble in water. When water enters gasoline, its amount with respect to gasoline can be very small and the concentration of acids in the water can reach high values, which entails the corrosion of the metal container.

The corrosiveness of organic acids was studied by I. Ye. Bespolov [21], L. G. Gindin and V. A. Kazakova [22], K. F. Prutton [6], and others. The results can be summed up as follows. The corrosiveness of acids with respect to magnesium and lead increases with an increase in the molecular weight of the acid. However, it rises unevenly: the weight loss of the magnesium increases by twofold with the transition from acetic acid to propionic acid, and by more than eight times with the transition to butyric, valeric, and capric acids in whose solutions the losses remain practically at the same level [22]. The presence of oxygen or peroxide is a necessary condition for the corrosion of lead and cadmium in hydrocarbon solutions of fatty acids [6]. The presence of moisture is secondary in importance [6].

As the result of metal corrosion caused by organic acids, salts are formed; their content depends on the kind of metal, solvent, acid, and its concentration, and so on. Thus, when magnesium is corroded with acetic acid in benzene solution a neutral salt is formed, but when this corrosion occurs in isooctane solutions an acid salt is formed. But when magnesium and lead are corroded with propionic and capric acids at their lower concentrations in isooctane, neutral salts are formed, while if this corrosion occurs at the higher concentrations of these acids, acid salts are formed. The acetic acid corrosion of magnesium in a solution of paraffinic hydrocarbons is more than twice as intense as in benzene [22].

The solubility of corrosion products in a gasoline depends on the molecular weight of the acid. With an increase in this molecular weight, the solubility of salts in gasoline improves. In soluble corrosion products are deposited on the walls of the container or remain in a suspended state. In the latter case, on entering together with the gasoline they are capable of plugging the filters or jet nozzles of a carburetor and thus causing engine misfires [23]. Corrosion products deposited on metal in the form of a film protect the metal against further corrosion and in this respect have a positive role. Thus, after removal of corrosion products, a zinc plate placed in gasoline loses 1.5 times more weight in 48 hours than in 1.5 months of storage [24].

A relationship between the content of organic acids formed in gasoline and the corrosiveness of the gasoline was noted in studies by I. Ye. Bespolov [25], L. G. Gindin [24, 26-30], R. A. Lipshteyn [3], M. K. Tikhonov [31, 32], I. N. Putilova [33], S. Bentur, M. Babits, and A. Stern [34].

Table 87. Corrosion of lead by cracking gasoline [24]

Продолжительность хранения, сутки 1	Содержание фактических смол, мг/100 мл 2	Кислотность, мг КОН/100 мл 3	Потеря массы металла, г/100 см² 4
535	124	4	0,6
528	178	9	1,1
528	203	11	1,6
535	325	21	2,6
710	1000	208	13,2

Key: 1 -- Storage time, days
2 -- Existent gum content, mg/100 ml
3 -- Acidity, mg KOH/100 ml
4 -- Weight loss of metal, g/100 cm^2

L. G. Gindin [24] presents data on the corrosion of lead with thermal cracking gasolines exhibiting different acidities due to the oxidation of unsaturated compounds in prolonged storage (Table 87). These results are of interest since at the present time many fuel tanks of domestic vehicles are made of steel coated with a thin layer of lead alloy.

R. A. Lipshteyn [3] concluded that one of the reasons for the rusting of steel and the oxidation of other metals from which gasoline containers are made is the oxidation of these metals by the "ageing" products of cracking gasoline, in all probability peroxide radicals or hydroperoxides. High corrosiveness of peroxide compounds was noted by G. S. Shimonayev, who stored straight-run fuel to which stable peroxide compounds had been added.

To find the relative role of peroxide compounds and acids in the corrosion process, this author undertook to study the corrosiveness of diisobutylene that had been previously oxidized in bombs to determine the induction period. The oxidation was carried out at 100° C and a 7 atm oxygen pressure for 40, 80, and 100 minutes (Table 88).

As oxidation products accumulate in diisobutylene, its corrosiveness rises. Oxidized diisobutylene severely corrodes a steel plate even at relatively low temperatures (40° C). Corrosion of the metal is accompanied by the consumption of oxidation products, and as this occurs the acidity and the peroxide number of diisobutylene becomes smaller.

The decrease in the acidity and the peroxide number (cf. Table 88) after corrosion tests is especially noticeable in strongly oxidized

Table 88. The effect of preliminary oxidation of diisobutylene on its corrosiveness

Показатель 1	Время предварительного окисления, мин 2		
	40	80	100
Коррозия, $г/м^2$, за 2 ч 3			
при 40° С 4	3,5	16,6	20,4
» 70° С 5	7,9	26,8	34,1
Кислотность, мг KOH/100 мл 6			
до коррозионных испытаний 7	7,0	59,0	72,5
после коррозионных испытаний 8			
при 40° С 4	8,1	17,8	32,1
» 70° С 5	5,4	24,5	25,6
Перекисное число, мг O_2/100 мл 9			
до коррозионных испытаний 10	24,2	31,0	78,3
после коррозионных испытаний 11			
при 40° С 4	25,3	30,1	53,9
» 70° С 5	25,1	22,6	42,7

Key:
1 -- Indicator
2 -- Preliminary oxidation time, minutes
3 -- Corrosion, g/m^2, in 2 hours
4 -- at 40° C
5 -- at 70° C
6 -- Acidity, mg KOH/100 ml
7 -- before corrosion tests
8 -- after corrosion tests
9 -- Peroxide number, mg O_2/100 ml

10 -- before corrosion tests
11 -- after corrosion tests

diisobutylene. Less oxidized diisobutylene is oxidized itself in the experimental conditions and less of the oxidation products are consumed in the corrosion reactions (the corrosion of metal in this compound is less than in severely oxidized diisobutylene).

Similar results were obtained with B-70 gasoline when gummy compounds were added to it. The gums were isolated from thermal cracking benzene by percolation through aluminum oxide. The corrosiveness of the gasoline rises with increase in its gum contents. The acidity of the gasoline becomes less in the corrosion tests.

To observe the combined changes in the content of oxidation products in gasolines and their corrosiveness, an experimental storage of three

Table 89. Change in the content of oxidation products in gasoline and change in corrosiveness when gasoline was stored in a thermostat at 40-45° C

Продолжительность хранения, месяцы A	Содержание фактических смол, мг/100 мл B	Кислотность, мг KOH/100 мл C	Коррозия стальной пластинки, г/м² (70 °C, 4 ч) D
Бензин термического крекинга E			
0	4,8	0,5	2,5
1	6,2	0,4	3,6
2	14,8	0,6	3,4
3	22,8	1,2	3,8
6	64,6	1,8	6,0
Бензин A-66 F			
0	3,6	0,2	4,0
1,5	6,4	0,2	4,0
3	6,0	0,2	3,5
9	31,8	0,4	4,6
Бензин A-72 G			
0	2,8	6,6	2,0
3	4,2	0,4	2,8
6	3,8	0,4	4,0
9	8,2	0,8	4,0
10	12,0	1,0	4,6
12	14,4	1,6	9,5

Key: A -- Storage time, months
B -- Existent gum content, mg/100 ml
C -- Acidity, mg KOH/100 ml
D -- Corrosion of steel plate, g/m^2 (70° C, 4 hours)
E -- Thermal cracking gasoline
F -- A-66 gasoline
G -- A-72 gasoline

gasoline samples was carried out in 3-liter glass bottles in a thermostat at 40-45° C. The results (cf. Table 89) showed that during storage, along with the increase in the gum content in gasolines, gasoline corrosiveness also rises. However, the gum content reaches the maximum attainable values (15 mg/100 ml -- for A-66 gasoline, and 10 mg/100 ml -- for A-72 gasoline) much earlier then the corrosiveness begins to rise markedly (Table 89).

Thus, a limitation on the extent gum content in commercial gasoline simultaneously presents a sharp rise in the corrosiveness of gasolines in storage. For a certain storage time dictated primarily by the increase in the gum content, the corrosiveness of most commercial automotive gasolines varies only slightly.

The above-presented data once again confirm the validity of the principle that for metals to corrode it is necessary that a gasoline contain not only organic acids, but also oxidizing agents. The corrosion process apparently consists of two stages: in the first the oxidizing agent, on reacting with the metal, produces the corresponding oxide, and in the second -- the oxide reacts with the organic acid -- it dissolves in it [23].

Peroxides and their decomposition products, as well as molecular oxygen, are oxidizing agents in gasolines. Thus, oxidation of unstable compounds leads to the formation of all the ingredients responsible for the corrosiveness of automotive gasolines.

Effect of Sulfur Compounds

Virtually all classes of organic sulfur compounds can be present in automotive gasolines. The specifications for automotive gasolines stipulate the total sulfur content regardless of the content of individual classes of organic sulfur compounds. This summary of content norm for sulfur compounds is obviously justified from the standpoint of the corrosive action of the combustion products of organic sulfur compounds. All sulfur compounds burn to SO_2 and SO_3, which then corrode automotive engine parts.

In conditions of transportation, storage, and use, the corrosiveness of gasoline depends not only on the total content of sulfur compounds, but also on their structure. The absence of investigations in this area has thus far presented a differentiated approach to setting norms for the content of sulfur compounds in commercial gasolines.

Of the compounds of so-called active sulfur, hydrogen sulfide, elementary sulfur, and mercaptans can be present in gasoline distillates. Existing methods of scrubbing and alkali wash of automotive gasoline components [35-38] ensure a negative test of commercial gasolines for copper strip corrosion according to GOST 6321-52. Based on the results of a study made by A. S. Eygenson and E. P. Toporova [39], the negative copper strip test covered by GOST 6321-52 shows that the hydrogen sulfide content in gasoline may not be more than 0.0003 percent, while the elementary sulfur content is not more than 0.0015 percent. This determination of the hydrogen sulfide content in automotive gasolines and their components governed by GOST 9558-60 showed that hydrogen sulfide is absent in commercial gasolines meeting the requirements of the standards [19].

A study of the role of elementary sulfur in the corrosion process was made [19] with B-70 gasoline and diisobutylene. The latter is convenient for this purpose, since it contains absolutely no sulfur compounds, and it readily oxidizes, forming fairly stable peroxide compounds and acids. The data (Fig. 124) showed that elementary sulfur intensifies the corrosion of steel and copper plates and has a weak effect on the corrosion of brass (Fig. 124). The corrosiveness of elementary sulfur begins to become clearly evident at a concentration about 0.0015 percent (Fig. 124). The corrosion of a steel plate in 4 hours remains within the limits of the acceptable norm (up to 4.5 g/cm^2) for an elementary sulfur concentration to 0.0015 percent.

Thus, the maximum allowable concentration of elementary sulfur in commercial gasolines can be taken as 0.0015 percent by weight. We have already stated earlier that a negative copper strip test ensures an elementary sulfur content of less than 0.0015 percent. In other words, the role of elementary sulfur is extremely small in the general corrosiveness of commercial automotive gasolines. An investigation of other organic sulfur compounds showed that their corrosiveness depends on concentration (Fig. 90).

Such organic sulfur compounds as sulfides, disulfides, thiophan, and thiophene, even in a relatively high concentration (0.1 percent S) somewhat decrease the corrosiveness of diisobutylene on steel plates. Obviously, the presence of this kind of organic sulfur compound in automotive gasolines does not play an appreciable role in the their corrosiveness. The mercaptans investigated in small concentrations somewhat reduce the corrosion of steel plates. At a 0.1 percent S concentration, all mercaptans intensify corrosion. The allowable content of mercaptans depends to a large extent on their structure. For example, n-octylmercaptan increases corrosion even at a concentration of 0.001 percent S, and for phenylethylmercaptan, a concentration of 0.001 percent S is obviously the maximum; higher concentrations can be allowed for other mercaptans without a detectable rise in corrosion.

It must be noted that the corrosiveness of mercaptans depends not only on the structure, but also on the oxidizability of the hydrocarbons in which they are dissolved. It was earlier noted that during the oxidation of unsaturated hydrocarbons mercaptans act an inhibitors; initiation of the oxidation of the mercaptans as such occurs. The accelerated oxidation of mercaptans leads to the accumulation of oxidation products and an increase in corrosiveness.

The results of investigating the comparatively corrosiveness of isooctane and cyclohexene in the presence of phenylethylmercaptan (0.05 percent S) showed that adding mercaptan to cyclohexene causes much more corrosion (in g/m^2) than adding it to isooctane [19]:

Isooctane	3.8
Isooctane + phenylethylmercaptan (0.05 percent S)	5.0
Cyclohexene	7.5
Cyclohexene + phenylethylmercaptan (0.05 percent S)	15.7

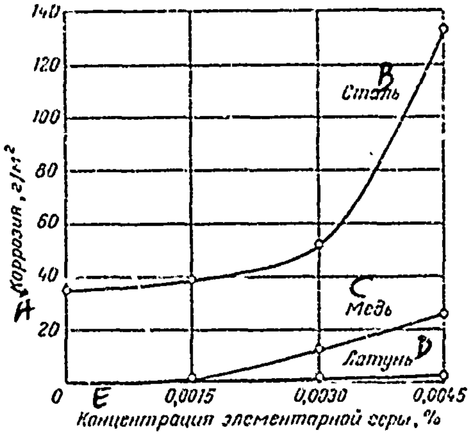


Fig. 124. Effect of elemental sulfur on the corrosiveness of B-70 gasoline in the presence of metals; temperature 70° C, experimental period 15.5 hours
Key: A -- Corrosion, g/m^2
B -- Steel
C -- Copper
D -- Brass
E -- Concentration of elemental sulfur

Obviously, in the case of cyclohexene the increase in corrosion occurred owing to the corrosiveness not only of the initial mercaptan, but also of its oxidation products.

Mercaptans of the most diverse structure can be present in commercial automotive gasolines. To estimate the allowable content of mercaptans in commercial automotive gasolines, a simultaneous determination was made of the mercaptan content and the corrosiveness for a number of fresh samples of gasolines of various origins [19].

The effect of mercaptans on fuel corrosiveness is indicated below:

	Mercaptan-sulfur content, percent	Corrosion, g/m^2
Catalytic cracking gasoline	0.0077	2.9
Thermal reforming gasoline	0.0267	8.9
Thermal cracking gasoline, sample 1	0.0058	2.5

[Continued on following page]

Table 90. Effect of organic sulfur compounds on the corrosiveness of diisobutylene (experimental period 4 hours at 70° C)

Соединение 1	Коррозия, г/м², при содержании сероорганических соединений 2				
	0%	0,0001%	0,001%	0,01%	0,1%
н-Октилмеркаптан 3	7,3	6,6	10,0	10,5	11,4
Фенилэтилмеркаптан 4	7,6	7,3	7,7	8,2	13,2
Пропилмеркаптан 5	7,3	6,4	7,0	8,5	11,8
Гексилмеркаптан 6	7,3	5,2	7,3	8,5	11,8
Изоамилмеркаптан 7	8,6	5,5	7,0	7,9	13,2
Диизопропилдисульфид 8	7,5	3,4	5,0	5,1	6,6
Дибутилдисульфид 9	8,8	6,0	5,9	6,3	8,2
Дибутилсульфид 10	7,7	4,5	4,3	5,9	5,5
Диизопропилсульфид 11	8,1	5,6	5,8	6,2	6,0
Тиофан 12	7,3	5,2	5,2	5,5	[illegible]
Тиофен 13	7,9	5,2	5,2	6,1	6,8

Key: 1 -- Compound
2 -- Corrosion, g/m², at indicated content of organic sulfur compounds
3 -- n-Octylmercaptan
4 -- Phenylethylmercaptan
5 -- Propylmercaptan
6 -- Hexylmercaptan
7 -- Isoamylmercaptan
8 -- Diisopropyl disulfide
9 -- Dibutyl disulfide
10 -- Dibutyl sulfide
11 -- Diisopropyl sulfide
12 -- Thiophan
13 -- Thiophene

	Mercaptan-sulfur content, percent	Corrosion, g/m²
Thermal cracking gasoline, sample 2	0.0102	4.5
B-70 gasoline	0.0003	2.2
A-76 gasoline	0.0013	1.8
A-72 gasoline, sample 1	0.0008	2.0
A-72 gasoline, sample 2	0.0041	4.0
A-66 gasoline, sample 1	0.0085	4.2
A-66 gasoline, sample 2	0.011	6.2

[Continued on following page]

	Mercaptan-sulfur content, percent	Corrosion g/m^2
A-66 gasoline, sample 3	0.0090	4.6
A-66 gasoline, sample 4	0.0068	4.4
A-56 gasoline	0.0095	4.5
Ekstra gasoline	0.0032	2.2

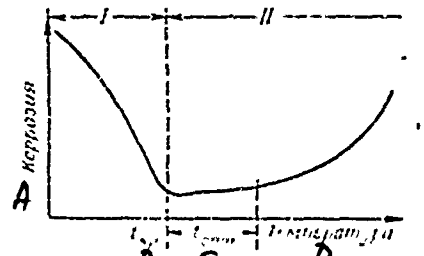
This investigation showed that gasolines containing less than one-hundredth of a percent mercaptan sulfur have low corrosiveness (up to 4.2-4.6 g/m^2). Thus, to prevent users from receiving corrosive gasolines of the thermal reforming gasoline type, we must limit the content of mercaptan sulfur in commercial automotive gasolines to not more than 0.01 percent, as already been done in diesel fuels according to GOST 305-62. The potentiometric method of determining the mercaptan-sulfur content in diesel fuels is suitable for a check on mercaptan-sulfur content. The suitability of this method for analyzing automotive gasolines has been verified [19]. Individual mercaptan boiling in the limits of gasoline fractions were added to hydrocarbon blends containing unsaturated hydrocarbons, and the mercaptan-sulfur content was determined by the potentiometric method. The results indicate that the method is entirely suitable for the analysis of automotive gasolines.

Corrosion by the Combustion Products of Sulfur Gasolines

The division of sulfur compounds in gasolines into active and inactive, as indicated above, is valid only for the period of fuel storage and transporting. During the combustion of the air-fuel mixture in the engine, all sulfur compounds form the strongly corrosive oxides of sulfur SO_2 and SO_3.

The corrosive action of sulfur oxides on metals can show up at different temperatures (Fig. 125). At a relatively low temperature when the condensation of water vapor from the combustion products is possible, electrochemical corrosion occurs under the action of sulfuric or sulfurous acids (the dissolution of SO_2 and SO_3 in water proceeds very rapidly). The range of low-temperature electrochemical corrosion in Fig. 125 is noted with the I.

At temperatures above the critical value, moisture does not condense on the surfaces and high-temperature dry gaseous chemical corrosion takes place (zone II, Fig. 125). There is a region of optimal temperatures where the corrosion is at a minimum. It must be noted that the decrease in temperature below the optimal value leads to a sharp rise in the rate of electrochemical corrosion, while gaseous corrosion increases not as rapidly with rise in temperature. Thus, from the standpoint of the corrosiveness of the combustion products of organic sulfur compounds, high-temperature



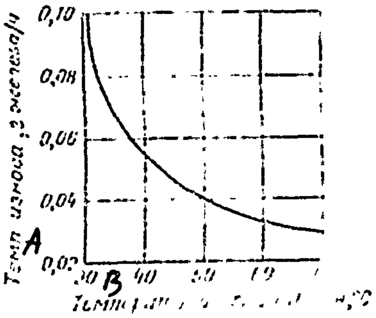


Fig. 125. Corrosion in combustion chamber as a function of temperature of corroded surface (t_{cr} and t_{op} are the critical and optimal temperatures)
Key: A -- Corrosion
B -- t_{cr}
C -- t_{opt}
D -- Temperature

Fig. 126. Effect of cooling temperature on engine wear rate
Key: A -- Wear rate g ion/hour
B -- Cooling temperature

regimes are less dangerous than low-temperature regimes. This is confirmed by numerous experimental data. Thus, from the data of N. P. Voinov and Yu. S. Zaslavskiy [40], a decrease in the engine cooling system temperature increases the rate of engine wear by more than three times (Fig. 126). In operating practice it has been noted that under otherwise equal conditions, corrosion has a smaller effect on cylinder wear for air-cooled engines than for water-cooled engines. In carburetor engines, corrosion more strongly affects cylinder wear than in compression-ignition engines. The greatest role of corrosive processes in general engine wear is observed in the starting of an engine, especially in winter, when it is operated with partial and prolonged stops.

In this respect, the results of an extensive study of gasolines with different sulfur content with the operation of 62 vehicles for 4.5 years are revealing [41]. All the test gasolines were divided into two groups: low-sulfur (sulfur content from 0.063 to 0.140 percent) and high-sulfur (sulfur content from 0.256 to 0.290 percent). It was noted that the service life of the mufflers and the corrosion of the exhaust system for both groups of gasolines were roughly the same. On the other hand, wear of piston rings and cylinder liners for engine operation on high-sulfur gasolines in conditions of low loads and frequent starts was 2-5 times higher than for low-sulfur gasolines.

To protect engine parts against corrosion when a vehicle is brought in for preservation, it is recommended to coat the piston heads, combustion chamber walls, and cylinder walls with special preservative oils.

The corrosiveness of the combustion products of sulfur gasolines depends strongly on the ratio of the sulfur oxides SO_2 and SO_3 that were formed. Both oxides are corrosive compounds, but the higher oxide SO_3 is more corrosive. For example, in the literature it was noted that whereas in the presence of SO_2 piston wear increases by four times, adding SO_3 in an amount that is one-third of the SO_2 content increases ring wear by 40 times [42].

There is no common view as to the quantitative ratio of sulfur oxides and the mechanism by which the higher oxide is formed. Some workers believe that from 60 to 90 percent of the sulfur contained in gasolines burns to SO_3 [42]; others [43] maintain that all the sulfur burns to SO_2 and that SO_3 is the product of subsequent catalytic oxidation of SO_2:

$$SO_2 + 1/2O_2 \rightleftarrows SO_3$$

Some SO_3 can form by the catalytic action of the metal of the cylinder walls. Nor is the homogeneous oxidation of SO_2 in flame to be precluded.

Numerous analyses of exhaust gases showed that the SO_3 detected in them to a large extent depends on the location and method of sampling the gas. Obviously, the conversion of the lower oxide to the higher can occur not only on exposure to the metal of the combustion chamber walls, but also along the entire route of the gases to the sampling location. So determining the ratio of SO_2 and SO_3 in the gas sample does not provide a full notion of the actual levels of sulfur trioxide formation [44].

The presence of SO_3 in combustion products is reflected in the temperature at which the gases begin to condense. A system of two components H_2O-H_2SO_4 has a higher condensation-onset temperature than water vapor. A significant rise in this indicator occurs even at ever low H_2SO_4 content. Thus, the critical wall temperature at which acidic corrosive products begin to condense rises markedly, when small amounts of SO_3 are present. In this case, the temperature range of the corrosiveness of combustion products is increased.

All measures reducing SO_3 formation in combustion products lead to reduced corrosion. Thus, the addition of ammonia to the combustion chambers of diesel engines proposed by B. V. Losikov [23] reduces SO_3 formation and lowers the corrosive wear of engine parts. Certain nitrogen-containing fuel additives have the same kind of action [45].

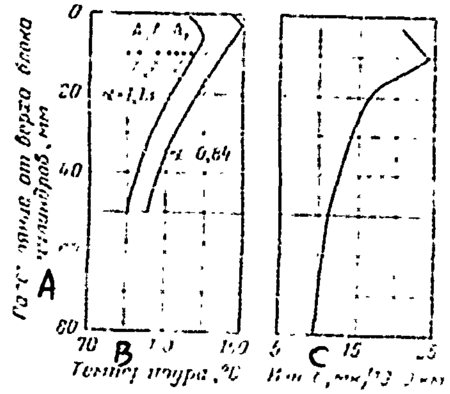


Fig. 127. Temperature of saturated vapor pressure and wear of cylinder walls for operation on a ga line containing 0.2 percent S, based on the piston travel at full load:

A_1, A_2, and A_3 -- the temperatures of walls 4, 5, and 6 of cylinders, at 2100 rpm

A_1', A_2', and A_3' -- as above, at 700 rpm

Key: A -- Distance from top of cylinder block, mm
B -- Temperature
C -- Wear, microns/1000 km

The main object of low-temperature corrosion caused by combustion products is the engine cylinder-piston group [46-50]. The possibility of water vapor or sulfuric acid condensing depends primarily on the temperature of engine parts, varying continuously during engine operation. Studies showed that the condensation of combustion products and the formation of an electrolyte film are most probable in the upper part of a cylinder. Owing to the high nonuniformity of temperature distribution along the peripheries that is typical for this part of the cylinder, condensation can be local, that is, it can occur only over those sections whose temperatures below the critical. The extent and distribution of the sections are determined by engine design characteristics. Thus, for carburetor engines with monolateral arrangement of valves in the block, the zone of the lowest temperatures in the upper part of a cylinder is situated opposite the valves, and because of this the zone is most severely humidified by the condensate and subject to corrosion [43].

The coincidence of the sites of possible condensation of combustion products and the greatest extent of corrosion wear is particularly well

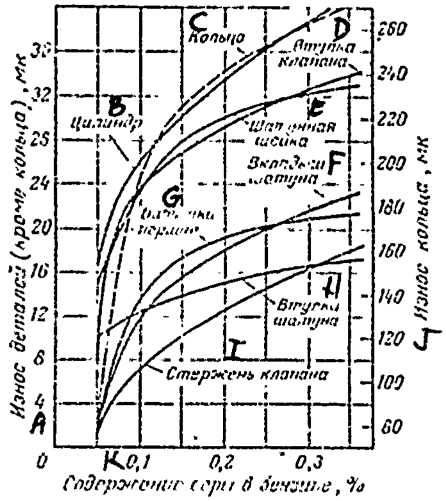


Fig. 128. Effect of sulfur content in gasoline on wear of Moskvich engine parts after 210 hours of operation on the stand

Key: A -- Wear of parts (except for ring), microns
B -- Cylinder
C -- Ring
D -- Valve head
E -- Connecting rod neck
F -- Connecting rod shell
G -- Piston boss
H -- Connecting rod insert
I -- Valve stem
J -- Ring wear, microns
K -- Sulfur content in gasoline

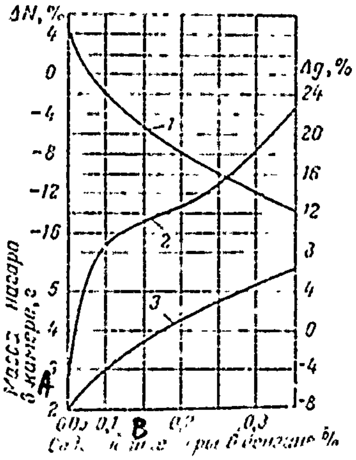


Fig. 129. Effect of sulfur content in gasoline on efficiency of Moskvich engine after 210 hours; stand tests:

1 -- loss in engine power Δ N
2 -- increase in fuel consumption g
3 -- Change in amount of deposits in combustion chamber

Key: A -- Mass of deposits in chamber, g
B -- Sulfur content in gasoline

illustrated by the data in Fig. 127 obtained from studies on the GAZ-51 engine [46, 47]. At 2100 rpm on lean mixtures, the cylinder walls 20 mm from the top had temperatures below the critical and it is precisely in this region that combustion products may condense. At 700 rpm this region is extended to 40 mm from the top of the cylinder block. The wear lines and saturation temperatures show a very similar trend (Fig. 127).

Numerous investigations both in our country as well as abroad established that wear of engine parts increases with sulfur content in gasoline.

Tests lasting 150 hours on low-liter one-cylinder air-cooled engines showed that on the sulfur content in gasoline is increased, cylinder walls and the piston rings wear out most intensively — the parts that are directly exposed to the corrosive medium. Here increasing the sulfur content from 0.05 to 0.1 percent causes a 1.5-2 times rise in wear. Raising the sulfur content from 0.1 to 0.2 percent causes a further 1.5-2 times increase in extent of wear. An increase in wear of 30-70 percent corresponds to a further increase in the sulfur content from 0.2 to 0.3 percent [47]. Similar results were obtained in 210-hour tests of four Moskvich vehicles on gasolines with different sulfur content (Fig. 128). Wear rises most intensively when the sulfur content is raised from 0.05 to 0.1 percent. Increasing the sulfur content in fuel from 0.05 to 0.2 percent increased the wear on the main parts by two to three times.

An immediate practical result of the corrosive action of sulfur on an engine is the deterioration in the power and economic indicators of engines resulting from the wear on parts, disturbances of the initial adjustments, and worsening of the working process owing to intense carbon deposits [47].

Results of estimating the engine power and fuel consumption by Moskvich engines after 210-hour testing are given in Fig. 129. For a minimum sulfur content in the fuel, there was no noticeable deterioration of engine indicators at all, compared with the initial values. With a further rise in the sulfur content in the gasoline to 0.2 percent, an 8 percent power loss and a 12 percent increase in specific consumption were observed. A further increase in the sulfur content caused growing deterioration in the engine working indicators.

With increase in the sulfur content in the gasoline, the deposits increase in proportion (cf. Fig. 129); there is higher acidity of the working oil and higher coke, ash, and iron content in it. Oxidized and polymerized products precipitate from the oil into sediment, forming sludge and other deposits [47].

Williams [44], on investigating the effect of sulfur content in gasoline on the wear of cylinder liners and piston rings for a 1-cylinder engine, found that an increase in sulfur content from 0.01 to 0.08 percent increases wear by about twofold.

Wear in a Chevrolet engine at a 35° C temperature proved to be a linear function of the change in sulfur content in the gasoline from 0 to 0.4 percent. When the sulfur content was raised from 0 to 0.1 percent, wear increased by twofold [50].

These data indicate that the total sulfur content in gasolines has a very appreciable effect on the longevity of an automotive engine.

High-octane gasolines are prepared with the incorporation of low-sulfur platforming products, and therefore in the future, with advances made in the refining industry, the problem of purifying automotive gasolines from the sulfur will obviously lose its urgency.

Anti-corrosion Additives

Most commercial automotive gasolines with restricted mercaptan-sulfur content at the time they are supplied from the refinery have relatively low corrosiveness. All anti-oxidants added to gasoline at the refineries prevent corrosive oxidation products from forming and thus also improve the anti-corrosion properties of gasolines. Using such gasolines in ordinary climatic conditions as a rule is not accompanied by significant corrosion of the containers, fuel lines, fixtures, and so on.

However, when automotive gasolines are used in high-humidity regions and also in the humid times of the year, the control of corrosion occurring in metals that are in contact with gasolines becomes vital. In these conditions often a film of moisture is formed on metal surfaces; as indicated above, this film severely accelerates corrosion processes. To reduce the corrosiveness of automotive gasolines, a special anti-corrosion additive can be used.

According to the proposed mechanism of action, specifically anti-corrosion additives can be conditionally divided into two groups [23]:

-- additives that chemically or catalytically reduce oxidizing agents or that neutralize acidic compounds; and

-- additives protecting metal surfaces with a film.

The ability to decompose peroxide compounds by reduction is shown by certain organic sulfur compounds. Therefore it is not fortuitous that sulfur is included in the composition of numerous anti-corrosion additives. Neutralization of acidic corrosive compounds can be achieved by adding compounds with basic properties, in particular, certain amines, and so on.

Underlying the action of most anti-corrosion additives is the formation of protective films. A protective film can be formed either by chemical reaction of the additive with the metal, or due to the surfactant properties of the additive, forming a layer (barrier) due to oriented adsorption of polar groups [23]. The formation of these protective films is essentially also a corrosion process, therefore the use of these additives is possible given the condition that:

-- the film will be bound strongly enough to the metal -- it will not flake off; and

-- molecules of compounds comprising the film will be resistant to external factors.

In terms of the kinetic mechanism of action, anti-corrosion additives are subdivided into immunizers, inhibitors, and passivators [30]. Immunizers include compounds whose addition to gasolines prolongs the induction. Before the onset of intensive corrosion; inhibitors slow down the corrosion rate, but do not extend the induction period, while passivators prevent corrosion at the very outset, by forming a protective film of corrosion products on the metal surface [44]. Many compounds of the most diverse classes have been investigated and proposed as anti-corrosion additives for gasolines [51-61].

Aminoalkylphosphates have found use as neutralizing anti-corrosion additives for gasolines. They are the products of the reaction of aliphatic branches amines (C_4 - C_{15}) and alkylphosphates (C_8 - C_{16}) and contain excess amine [59]. Aliphatic amines can be replaced in this additive by certain imidazoles. The recommended concentration of aminoalkylphosphates is 0.002-0.05 percent [23].

Anti-corrosion additives with surfactant properties are found among the fatty acids with long chains, esters, diesters, salts of fatty and naphthenic acids, oxycarboxylic acids, amines, and other compounds [51, 52].

Certain thio-, chloro-, and amino-derivatives of fatty and aromatic hydrocarbons exhibit high protective properties [61]; sulfonated stearic acid, chlorinated paraffin, and diphenylamine were tested [61]. Some of these compounds protect steel against corrosion for one year and longer.

Preventing the corrosion of metals by ethyl gasolines is achieved by adding the sodium salt of methoxydisulfamido acetic acid

$$CH_3(CH_2)_{11-17}SO_2NHCH_3COONa$$

in the amount of 0.05-0.1 percent [53]. The additive is soluble in gasoline and water. Owing to its surfactant properties, it is distributed in a thin layer on metal, forming a protective film that can be restored when impaired.

Fluoride salts of alkali metals (sodium or potassium) and ammonium were found to be effective agents for protecting tanks and fuel systems from corrosion caused by ethyl gasolines; they are placed in the gasoline in cartridge form [53, 62].

No special additives have been developed to protect against corrosion caused by active sulfur compounds. However, it has been noted that in the corrosion of copper by sulfur in hydrocarbons is significantly retarded upon the addition of anthraquinone, aniline, triethanolamine, quinoline, benzyl alcohol, pyrogallol, alpha-naphthylamine, phthalic anhydride, phthalimide, and other compounds [30].

Table 91. Inhibition of corrosion in the presence of sulfur gasoline caused by inhibitors (experimental period 54 days) [63]

Концентрация ингибитора, % 1	Марка металла 2	Во сколько раз замедляется коррозия 3		
		над топливом 4	в топливе 5	на границе раздела вода и топливо 6
0,01	СХЛ-1 7	22	-- 11	13,5
0,01	СХЛ-4 8	Полная защита 11	Полная защита	3,7
0,01	4С 9	То же 12	То же 12	2.6
0,01	Л-62 10	—	61	—
0,02	СХЛ-1 7	Полная защита 11	Полная защита 11	6,0
0,02	СХЛ-4 8	2,6	То же 12	2,5
0,02	4С 9	2,4	»	6,1
0.02	Л-62 10	—	7,6	—
0,05	СХЛ-1 7	Полная защита 11	Полная защита 11	Полная защита 11
0,05	СХЛ-4 8	То же 12	То же 12	То же 12
0,05	4С 9	»	»	»
0,05	Л-62 10	—	2,9	—

Key:
1 -- Inhibitor concentration
2 -- Metal grade
3 -- By how many times corrosion was inhibited
4 -- over fuel
5 -- in fuel
6 -- at water-fuel interface
7 -- SKhL-1
8 -- SKhL-4
9 -- 4S
10 -- L-62
11 -- Complete protection
12 -- As above

An inhibitor based on ammonia and benzoic acid [AMBA] proved to be highly effective in protecting steels against corrosion by sulfur automotive gasolines (0.1 percent S) in the presence of water. Tests in operating conditions (in stationary vessels and tankers) showed its high effectiveness (Table 91). The inhibitor can be added directly to the gasoline, to the ballast sea water [63], or it may be splashed over the surface of an empty tank.

To prevent metals from rusting in the presence of water, a large number of compounds have been proposed, which are given the common name of rust inhibitors. They include, for example, salts f mepazinesulfamido acetic acids, p-dioxybenzophenone, the monoethyl ester of ethylene glycol N-acylamino acid, salts of naphthenic acids, and amino and ammonium sulfonates [51, 61]. In the presence of sea water it is recommended to use a mixture of alkylmercaptoacetic acid and the acid esters of lauryl- or dioctylphosphoric acids [61].

The action of rust inhibitors amounts to the additive film forming on the metal surface protected against the adhesion of water droplets [57]. The use of inhibitors considerably reduces the corrosion of fuel lines, pumps, fuel tanks, storage tanks, and other equipment. Tanks used for moving gasolines containing a corrosion inhibitor can be used for a number of years without special coatings [57]. Without the additive, on the average 6.3 kg of rust forms in each vehicle tank 4 m^3 in capacity, while in the same conditions an average of 0.93 kg of rust forms in tanks containing inhibited fuel in the same conditions [57].

Similar results confirming the effectiveness of rust inhibitors were obtained in a study made of vehicles operating on gasoline containing the additive. Corrosion was not observed in carburetors, pumps, and gasoline tanks of vehicles operating on inhibited gasoline. Cases of engine failure associated with fuel system plugging with corrosion products were completely ended. The need to replace carburetors and pumps was reduced by 75 percent [57].

At the present time several anti-corrosion additives for automotive gasolines have been developed and are in use in foreign practice:

	Concentration, percent by weight
Gulf Agent 178 (alkylamino-phosphate)	0.002-0.008
Masul LP (50 percent solution of ethylenediamine dinonyl-naphthalene sulfonate)	0.007-0.008
Dupont RP2 (25 percent octyl-ester of phosphoric acid, 55 percent octylamine, n-octyl alcohol, and 20 percent hydrocarbon diluent)	0.003-0.008
Tolad 244	0.002-0.008
Lubrisol Concentrate 531	0.002-0.006
Dupont AFA-1	0.002-0.007
Santolene C (dimerized linseed oil)	0.002-0.007
Unicor	0.003-0.008

No anti-corrosion additives have been developed for domestic automotive gasolines and similar studies have not been conducted in our country. The author tested the effectiveness in gasoline of several additives to lubricating oils exhibiting anti-corrosion properties to some

Table 92. Anticorrosive effectiveness of additives incorporated in catalytic cracking gasoline (experimental period 10 hours at 70° C)

Присадка 1	Коррозия, г/м² 2			
	3 без присадок	4 при концентрации присадки		
		0,005%	0,01%	0,05%
Сульфонат кальция 5	33,9	0,7	0,7	0,7
» бария 6	33,3	30,4	16,3	1,4
» натрия 7	35,9	3,0	3,2	1,6
» аммония 8	33,6	3,0	1,6	1,1
Нитрованное масло, нейтрализованное гидроокисью 9				
кальция 10	35,0	5,2	3,2	1,1
цинка 11	33,6	21,8	4,5	3,9
лития 12	33,1	5,7	2,3	1,1
алюминия 13	34,1	2,7	1,8	1,5
калия 14	32,7	11,1	0,2	0,2
бария 15	35,9	8,9	2,5	2,3
аммония 16	33,1	12,7	3,4	1,1
свинца 17	32,9	18,8	7,9	0,5

Key: 1 -- Additive
2 -- Corrosion, g/m^2
3 -- containing no additives
4 -- at the indicated additive concentration
5 -- Calcium sulfonate
6 -- Barium sulfonate
7 -- Sodium sulfonate
8 -- Ammonium sulfonate
9 -- Nitrated oil neutralized with the indicated hydroxide
10 -- Calcium hydroxide
11 -- Zinc hydroxide
12 -- Lithium hydroxide
13 -- Aluminum hydroxide
14 -- Potassium hydroxide
15 -- Barium hydroxide
16 -- Ammonium hydroxide
17 -- Lead hydroxide

extent. The results showed that in the presence of moisture anti-corrosion additives can significantly reduce the corrosion of steel strips. Among the oil additives investigated, the following compounds proved to be quite effective also in gasolines:

		Corrosion* g/m^2
Thermal reforming gasoline		7.9
containing	DF-1	2.1
"	DF-11	2.7
"	An-22k	1.1
"	IP-22k	2.5
"	SB-3	0.8
"	VNII NP-360	0.8
"	PMSya	0.8
"	TsIATIM-339	0.9
"	VNII NP-370	0.7
"	Santolube-493	4.8
"	NG-104	0.4
"	BFK	0.2

---

* After 4 hours at 70° C.

Two compounds -- sulfonates and nitrated oils -- underwent detailed testing as anti-corrosion additives for gasolines. The sulfonates were prepared by sulfonation of oils produced by selective purification with sulfur dioxide in liquid sulfur dioxide, followed by neutralization of the sulfo acids with alkali solutions [64].

The nitrated oils were prepared by treating selective-purification oils with nitric acid, followed by neutralization of the nitration products with alkali solutions [64].

The results of investigating several sulfonates and nitrated oils are given in Table 92. Among the compounds tested, those containing calcium, aluminum, and other metals prove to be the most effective.

Additives containing metals are of the ash type and use in engines can be accompanied by increased deposits.

Obviously, anti-corrosion additives for automotive gasolines must be sought for among nonash compounds.

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[To Chapter Eight]

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CHAPTER NINE

USE OF GASOLINES AT LOW TEMPERATURES

More than half of the territory of our country is occupied by regions with severe climatic conditions. Low air temperatures, sometimes with high winds, persist here for 7-10 months a year. Great natural wealth has been discovered over this enormous territory: petroleum, gas, diamonds, polymetallic ores, etc., which served as the cause of the rapid industrial development of these regions using large numbers of equipment, including also motor vehicle transportation.

The conditions for operating motor vehicles at lower temperatures imposed two main requirements on the quality of the fuels: good starting properties and the absence of crystal formation.

Low-Temperature Properties

When the temperature drops, microcrystals of ice or hydrocarbons can form in the fuel, turning the fuel cloudy. This temperature is commonly called the cloud point. With further cooling coarse crystals visible with the naked eye can appear in fuel. This temperature is customarily called the crystallization point. At a still lower temperature crystal coalescence occurs, and the fuel loses its fluidity. This temperature is called the pour point.

Crystals forming in the fuel at low temperatures can plug filters in the engine feed system and the supply of fuel can be blocked. The formation of ice crystals is associated with the solubility of water in fuels, and the formation of hydrocarbon crystals is associated with their pour point.

Water in gasolines. Water can be contained in gasolines in the dissolved state and has a second phase. A very small amount of water can be contained in gasoline in the dissolved state. Even in the most hygroscopic hydrocarbon -- benzenes -- in the solubility of water at 20° C is only 0.0582 percent. However, even in these amounts water dissolved in gasoline can cause disturbances in engine operation, especially at below-zero temperatures [1, 2].

The water content in automotive gasolines depends both on external conditions as well as on the chemical composition of gasoline itself. Aromatic hydrocarbons have the greatest dissolving ability with respect to water. This can be seen from the following data, where the solubility (in percent by weight) of water in various hydrocarbons is shown at 20° C:

Paraffinic hydrocarbons	
2-Methylbutane	0.0112
n-Hexane	0.0101
2,3-Dimethylbutane	0.0110
n-Heptane	0.0096
2-Methylhexane	0.0103
2,2,3-Trimethylbutane	0.0106
n-Octane	0.0095
2,4-Dimethylhexane	0.0008
2,2,4-Trimethylpentane	0.0115
2-Methyloctane	0.0090
3-Methyloctane	0.0087
2,6-Dimethylheptane	0.0091
2,7-Dimethyloctane	0.0087
Naphthenic hydrocarbons	
Cyclopentane	0.0142
Methylcyclopentane	0.0131
Ethylcyclopentane	0.0119
Isopropylcyclopentane	0.0102
n-Butylcyclopentane	0.0095
Cyclohexane	0.0122
Methylcyclohexane	0.0116
Aromatic hydrocarbons	
Benzene	0.0582
Toluene	0.0460
Ethylbenzene	0.0373
m-Xylene	0.0102
Isopropylbenzene	0.0303
1,3,5-Trimethylbenzene	0.0291
n-Butylbenzene	0.0331
sec-Butylbenzene	0.0317
per-Butylbenzene	0.0292
Diethylbenzene	0.0319
Unsaturated hydrocarbons	
2-Methylbutene-2	0.0435
Hexene-1	0.0477*
2,3-Dimethylbutene-1	0.0459*
Heptene-1	0.0249
Mixture of 3-Methylhexene and 3-Methylheptene	0.0401
Mixture of Octene-1 and Octene-2	0.0355
Di-isobutylene (technical)	0.0191
Cyclohexene	0.0317

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* At 30° C.

The largest amount of water is dissolved in benzene; as the molecular weight of aromatic hydrocarbons is increased, the solubility of water in them becomes smaller. A similar function is observed for paraffinic and naphthenic hydrocarbons. However, the effect of molecular weight in these hydrocarbon classes is less evident. Among paraffinic hydrocarbons, the solubility of water increases with increase in the branched character of a molecule. Napthenic hydrocarbons with alkyl side chains dissolve more water than the paraffinic hydrocarbons of normal structure corresponding to them in molecular weight, for the same molecular weight of comparison: derivatives of cyclohexane contain less dissolved water than the derivatives of cyclopentane. Unsaturated hydrocarbons are capable of dissolving much more water than their structural counterparts in the classes of paraffinic and naphthenic hydrocarbons [1].

When hydrocarbons of various structures are blended, the solubility of water in the blends varies according to additivity [1]. The more aromatic hydrocarbons in a gasoline, the higher is the amount of water it can dissolve (Fig. 130).

Among the atmospheric conditions, temperature and humidity have the greatest effect on the solubility of water in gasolines.

As the temperature of hydrocarbons and gasolines is decreased, the solubility of water therein becomes less (Fig. 131). The temperature dependence of the solubility of water in hydrocarbons and gasolines can be expressed by the empirical equation:

$$\lg c = A - \frac{B}{T}$$

where c is the content of water at temperature T, percent, and A and B are constants.

A reduction in humidity also leads to a decrease in the amount of water solubility in gasoline (Fig. 132). The water content in gasolines is directly proportional to the relative humidity:"

$$c = c_{max}$$

where c is the content of water at a given humidity, and c_{max} is the content of water at a relative humidity of 100 percent.

The dependence of the solubility of water on atmosphere is similar (cf. Fig. 132). The water content in gasolines is determined by the water vapor pressure or the fuel, therefore with a decrease in atmospheric pressure and a corresponding reduction in the water pressure, there is a decrease in the amount of water soluble in gasolines. Water dissolved in a gasoline

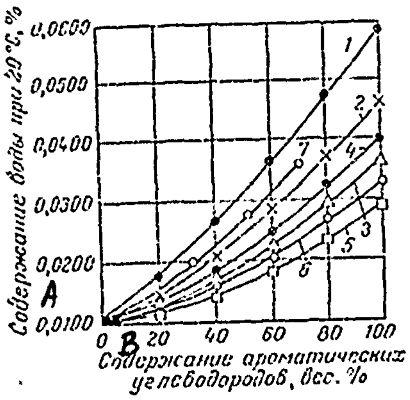

Fig. 130. Effect of aromatic hydrocarbon content in gasolines on the solubility of water therein at a 100 percent relative humidity:

1 -- Dearomatized straight-run + benzine
2 -- as above + toluene
3 -- as above + ethylbenzene
4 -- as above + para-xylene
5 -- as above + cumene
6 -- as above + sec-butylbenzene
7 -- Blends of straight-run gasoline with reforming gasoline

Key: A -- Water content at 20° C
B -- Content of aromatic hydrocarbons, percent by weight

is in a state of mobile equilibrium with the water contained in air [1-6]. And the transition of water from gasoline to air and from air to gasoline occurs quite rapidly. It has been established experimentally that for a fuel layer thickness of 5 mm, even in 30 seconds the water content in fuel reaches its maximum, determined by the temperature, humidity, and atmospheric pressure. For a fuel layer thickness of 15 mm, total saturation of fuel with water occurs in about 10 minutes, and for a thickness of 29 mm -- in 25-30 minutes. Numerous experiments showed that anhydrous fuel can quite rapidly be newly saturated with water. The rate at which fuel is saturated with water and water passes from fuel into air under otherwise equal conditions depends on the thickness of the fuel layer and on the ratio of the surface of the fuel-air contact to the volume of the fuel poured into a tank.

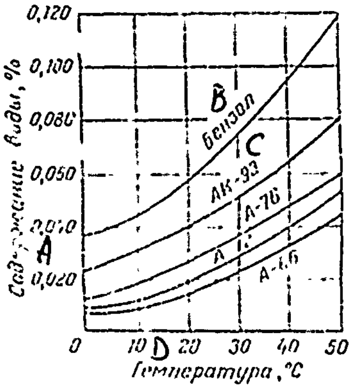

Fig. 131. Effect of temperature on the solubility of water in fuel
Key: A — Water content
B — Benzene
C — AR-93 gasoline
D — Temperature

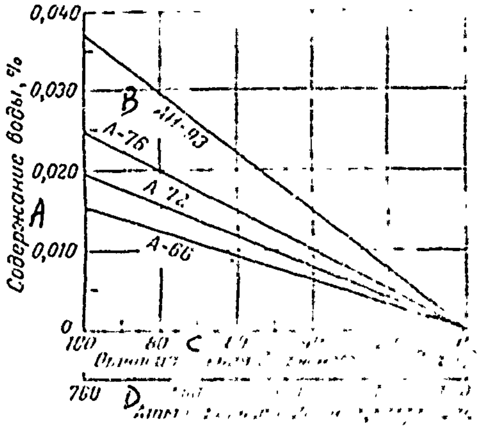

Fig. 132. Effect of relative humidity and atmospheric pressure on the solubility of water in gasolines
Key: A — Water content
B — AR-93 gasoline
C — Relative humidity
D — Atmospheric pressure,

In horizontal tanks the ratio of the area of fuel-to-air contact to the volume of the fuel is greater than in vertical tanks, therefore the water content in fuel in a horizontal tank changes more rapidly than in fuel poured into a vertical tank. In above-ground tanks th fuel temperature changes more than in underground tanks, which sets up conditions for convection currents to arise. Under their effect, the diffusion of water molecules in fuel intensifies, and so the water content in fuel in above-ground storage changes more rapidly than in underground storage. Thus, change in the temperature of gasoline and air, humidity, and atmospheric pressure leads to a change in the water content in gasoline. When there is a deficiency of water in a gasoline, moisture can be absorbed from the air, and in turn excess moisture from gasoline can pass into the air.

When there is a decrease in the temperature of air and gasoline, or a reduction in humidity, the amount of water that can be in gasoline in its dissolved state becomes less, and the excess water passes from the gasoline into the ambient atmosphere. If cooling of gasoline occurs very rapidly, then water during the cooling time is unable to pass from the gasoline into the air and is segregated as a second liquid phase. If desegregation of water from the gasoline occurs at below-zero temperatures, ice crystals form in the gasoline.

The formation of ice crystals is observed also in the condensation of water vapor on the surface of a gasoline whose temperature is below 0° C. These conditions are produced when there is rapid heating accompanied by a considerable increase in humidity. Usually, during cooling gasoline as a rule has a higher temperature than air, and with heating - the opposite is the case. Ice crystals can enter gasoline from without in the form of hoarfrost falling off the walls of vessels.

The segretation of water from gasoline into a second phase occurs at the outset in the form of minute droplets that are invisible to the naked eye. A further increase in the segregating droplets due to the collision and coalescence of fine droplets leads to clouding of the gasoline. Clouding of gasoline begins when the size of the segregating droplets exceeds 0.1 microns. The most minute mechanical impurities always present in gasolines play a key role in the formation of droplets of water and their coalescence.

Studies showed that at below-zero temperatures the formation of ice crystals is preceded by the segregation of water droplets. Water segregating from gasoline can exist for a long time in the supercooled state. Droplets of supercooled water can accumulate in gasoline and as a result of a slight external exposure precipitate as large numbers of ice crystals. An exposure of this kind can include hoarfrost falling into the gasoline, intense agitation, etc. The shape and size of ice crystals present in gasoline depend on the conditions of their formation and the presence of minute fibers or other mechanical impurities. These impurities are usually centers of the crystallization of water.

In the cooling of gasoline containing water droplets, initially individual fine rhombic-shaped ice crystals are formed, which with increasing cooling aggregate with the simultaneous inception of new ice crystals [1]. Upon prolonged presence of ice crystals in gasoline flocs are formed, which settle to the bottom of the vessel.

Ice crystals entering an engine's feed system are trapped by the filter, which leads to the partial, and then the complete plugging of the filtering partition and stoppage of gasoline feed into the engine. The composition of crystals plugging filters includesnot only water, but also gasoline, whic obviously is adsorbed on the surfaces of the ice crystals. Studies showed that crystals removed from the filter, when melted, yield two layers of water and fuel equal in volume. Here the fuel does not differ in fractional composition and other properties from the fuel in which the crystals were formed. Only the crystals that obviously entered the fuel in the form of hoarfrost from the sides of the tank contain fuel of lighter fractional composition [1].

In controlling the plugging of fuel filters by ice crystals, various design methods, procedures for dewatering fuels, and special additives eliminating crystal formation have been proposed. All these measures were developed for aircraft engines operating on gasoline or kerosene.

Adding special additives to fuel is the most effective method. Numerous compounds have been tested as additives, but alcohols, in particular, Ethyl Cellosolve [7] were found to be the most effective compounds.

Ethyl Cellosolve, when added to fuel in amounts up to 0.3 percent, prevent ice crystals from forming down to -60° C. This compound also has the ability to dissolve ice crystals previously formed. The action of Ethyl Cellosolve is accounted for by the fact that in its presence the solubility of water in fuel increases and fuel does not segregate out as a second phase. When a large amount of water accumulates in fuel, a second phase forms, however the segregating fuel in this case does not crystallize, since in the presence of Ethyl Cellosolve low-freezing mixtures are formed [7].

Ethyl Cellosolve $CH_2OHCH_2(OC_2H_5)$ is the monoethyl ester of ethylene glycole, a clear colorless liquid with a specific gravity of 0.930-0.935 g/cm^3 and index of refraction 1.4070-1.4090. Studies showed that in concentrations up to 0.3 percent, Ethyl Cellosolve does not affect the physicochemical and operating properties of fuels. Since Ethyl Cellosolve can be extracted from fuels with water, it must be added to fuel immediately before use. In foreign practice Methyl Cellosolve is used to prevent ice crystals from forming in fuels [8].

In conclusion it must be noted that the additives found extensive industrial use only for aviation fuels; no additives or any other agents preventing crystal formation are thus far used to prevent crystal formation in automotive fuels. Restricting the aromatic hydrocarbon content is one of the ways of reducing crystal formation in automotive gasolines.

Pour point of gasolines. Most of the hydrocarbons present in automotive gasolines solidify at very low temperatures (in ° C):

Paraffinic hydrocarbons		Naphthenic hydrocarbons	
n-Butane	-135.0	Cyclopentane	-93.3
Isobutane	-145.0	Methylcyclopentane	-140.5
Pentane	-129.7	Cyclohexane	+6.3
2-Methylbutane	-160.0	Methylcyclohexane	-126.3
2,2-Dimethylpropane	-16.0	Ethyldicyclohexane	-111.3
n-Hexane	-95.3	1,1-Dimethylcyclohexane	-146.7
2-Methylpentane	-153.7	1,2-Dimethylcyclohexane	-57.5
2,2-Dimethylpentane	-99.7	1,3-Dimethylcyclohexane	-85.0
2,3-Dimethylbutane	-129.8	1,4-Dimethylcyclohexane	-36.9
3-Methylpentane	-118.0		
n-Heptane	-90.6		
2-Methylhexane	-118.2		
3-Methylhexane	-119.4		

2,2-Dimethylpentane	-125.0
2,4-Dimethylpentane	-119.4
3,3-Dimethylpentane	-135.0
3-Ethylpentane	-118.7
2,2,3-Trimethylbutane	-25.0
n-Octane	-56.5
2,2,3,3-Tetramethylbutane	-102.2
2,2,3-Trimethylpentane	-112.3
2,2,4-Trimethylpentane	-107.4
2,3,4-Trimethylpentane	-110.0
2,5-Dimethylhexane	-90.7
2-Methylheptane	-111.3
n-Nonane	-53.7
2-Methyloctane	-80.5
3-Methyloctane	-108.0
4-Methyloctane	-119.3
n-Decane	-29.7
2-Methylnonane	-74.7
2,7-Dimethyloctane	-49.2
Undecane	-25.6
n-Dodecane	-9.6

Aromatic hydrocarbons

Benzene	+5.5
Toluene	-95.0
Ethylbenzene	-94.9
o-Xylene	-25.0
m-Xylene	-47.4
p-Xylene	+13.0
Durene	+80.0
n-Propylbenzene	-99.2
Isopropylbenzene	-96.9
n-Butylbenzene	-81.2
Amylbenzene	-78.3

Olefinic hydrocarbons

Hexene-1	-98.5
2,3-Dimethylbutene-1	-140.1
3,3-Dimethylbutene-1	-115.5
2,3-Dimethylbutene-2	-75.4
2,3,3-Trimethylbutene-1	-111.4
2,4,4-Trimethylpentene-1	-93.6
Cyclohexene	-103.7
2-Methylbutene-2	-124.0
2-Methylbutene-3	-135.0

Hydrocarbons with fairly high pour points, even if contained in gasolines, are present in very small amounts, and in mixtures with other hydrocarbons do not strongly influence the pour point. Therefore ordinarily automotive gasolines solidify at temperatures below -60° C and this operating indicator causes no trouble in operation.

Of the hydrocarbons with high pour points, benzene can be present in gasoline in the largest amount. The temperature at which benzene crystallizes in gasoline depends on the benzene content and the hydrocarbon composition of the gasoline. With increase in the benzene concentration in a gasoline, its crystallization begins at a higher temperature.

Crystalline benzene precipitates from solution in paraffinic hydrocarbons at a higher temperature than from a solution in aromatic hydrocarbons. Gasolines containing a mixture of hydrocarbons of different classes and also of varying capacity to maintain benzene in the solute state are intermediate in this respect [1]. The addition of aromatic hydrocarbons to gasoline lowers the benzene crystallization point.

Catalytic reforming (platforming) gasoline, which in recent years has found wide acceptance in compounding of high-octane gasolines, contains up to 70 percent aromatic hydrocarbons. There is relatively little benzene in these gasolines, but there are other hydrocarbons with fairly high crystallization points. The amount of such hydrocarbons in the tail fractions is quite high and this influences the crystallization point of the fractions. For example, the 180-240° C fraction of drastic-regime platforming gasoline contains 98 percent aromatic hydrocarbons and begins crystallizing at -25° C.

Platforming gasoline contains 2.5-3.0 percent benzene and it does not affect the crystallization temperature of the fuel. However, the 62-80° C fraction of this gasoline contains about 15 percent benzene and its crystallization-onset temperature is -49° C. The 80-90° C fraction contains 23 percent benzene and its crystallization-onset temperature for this fraction is -46° C. These data indicate the necessity of standardizing the crystallization-onset temperature of automotive gasolines, at least for northern and winter grades.

Starting fluids

Earlier, in Chapter Five, we examined the difficulties arising in starting a cold engine at low temperatures. Forming a combustible mixture capable of spark ignition depends on the volatility of the gasoline ore, in other words, on its content of low-boiling hydrocarbons. The content of these hydrocarbons can be increased only to a certain level, since when a warmed engine is running gasoline will evaporate in the fuel system, producing vapor locks. Therefore the idea was formed of starting an engine with special "starting" gasoline and then, even while it is running, switching the engine over to another gasoline with relatively poor starting qualities. Starting gasolines were used for a very short time and were replaced with special starting fluids, which have several advantages over starting gasolines. As for the difficulties associated with using a special starting fuel in the engine, they are about the same for gasoline as for the fluid.

<u>Composition and properties</u>. In recent years, several compositions of starting fluids were developed in our country and abroad, and extensive studies of their effectiveness in stand as well as in operating conditions were carried out [9-16]. However, most proposed fluids were intended for starting diesel engines and were designed for the specific features of precisely these engines. The domestic Arktika starting fluid was developed and thoroughly tested for carburetor engines; this fluid permits a cold engine to be started without preliminary warming down to an air temperature of -40° C [15, 16].

Table 93. Results of tests of various starting fluids in a refrigerated chamber on the ZIL-375 carburetor engine (ASZp-6 Oil)

Жидкость 1	Температура пуска, °C 2	3 Время пуска, сек	4 Число попыток
Дизельная 5			
марки А 6	—20	Не запускается 10	—
марки Б 7	—20	35	1
марки Б 8	—30	Не запускается 10	—
«Арктика» 9	—30	2,0	1
«Арктика» 9	—35	4,5	1
«Арктика» 9	—40	2,5	1

Key:
1 — Fluid
2 — Starting temperature
3 — Starting time, seconds
4 — Number of tries
5 — Diesel
6 — grade A
7 — grade B
8 — grade B
9 — "Arktika"
10 — Does not start

Attempts to use starting fluids for diesel engines to start carburetor engines have been unsuccessful (Table 93), obviously for the following reasons. Starting fluid for diesel engines must contain as high as content as possible of components reducing the self-ignition temperature of the fuel. It is for this very reason that up to 20 percent isopropyl-nitrate and diethyl ether is added to them.

There is no need to lower the self-ignition temperature of the starting fluid for spark-ignited engines. To reduce the wear on rubbing parts, in the initial period of diesel engine starting, often 10-60 percent lubricating oil is added to the starting fluid. The use of these fluids in spark-ignition engines leads to oil settling on sparkplugs, their becoming oiled, and misfires. And thus, starting fluids for carburetor and diesel engines must be of different kinds and their composition must correspond to the features of the working process in each of these engine types.

Components which prepare the combustible mixture for spark ignition are useful in fluids used with carburetor engines. These include several intermediate products of the oxidation of hydrocarbons (alcohols, aldehydes, and peroxides), as well as isopropyl nitrate, but in low concentrations. A valuable component of the starting fluid for carburetor engines was also found to be diethyl ether. However, here its role is fundamentally distinct from its role in diesel starting fluids. Diethyl ether greatly enlarges the limits to the ignition of the air-fuel mixture for different values of the excess air coefficient. Its addition to hydrocarbons permits the spark ignition of very lean mixtures which cannot be ignited without ether. The good volatility of ether is also important for the carburetor engine.

Natural gasoline is added as one of the main components to the starting fluid for carburetor engines. Earlier it was proposed to use individual hydrocarbons for such fluids, but they are expensive in mass production and, in addition, their rapid evaporation and ignition can lead to a sharp pressure rise in the cylinder, that is, a significant increase in roughness of engine operation and, as a consequence, to greater wear and even to fracture of parts. Natural gasoline boiling in the limits 30-70° C permits a more uniform evaporation and smooth buildup of pressure. The cost of natural gasoline is somewhat lower than the cost of individual hydrocarbons.

Special antiwear or antiseizure additives of the Sovol type, derivatives of xanthogenates, etc., are added to starting fluid to reduce the wear on rubbing parts in the initial period of the starting of a carburetor engine, and for stabilization in fuel transportation and storage, an anti-oxidant is used.

Based on the specific features of preparation of the working mixture and its combustion in spark-ignition engines, and also from the results of laboratory studies and stand tests, the following composition of starting fluid was selected for carburetor engines (in percent):

Diethyl ether	45-60
Natural gasoline	35-55
Isopropyl nitrate	1-5
Aldehydes, alcohols, ketones, peroxide compounds, etc.	Up to 10
Antiwear or antiseizure additives	Up to 2
Anti-oxidants	Up to 0.5

The effectiveness of the starting fluid depends on how it is introduced into the engine. The method of feeding starting fluids by spraying

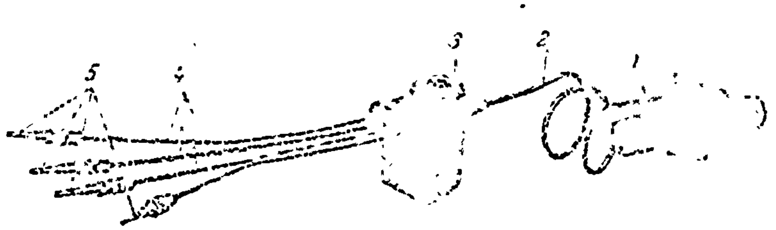

Fig. 133. Starting Accessory:
1 -- Air pump;. 2 -- Air line; 3 -- Chamber for
starting fluid; 4 -- Piping; 5 -- Nozzles

from aerosol cans directly into the air cleaner or the carburetor proved to be poorly suitable in practice for full-sized multicylinder engines. This method permits efficient use of the Arktika starting fluid only in one- and two-cylinder lower-liter engines.

The most efficient use of starting fluids for moderate and high-liter engines is achieved by introducing them into the intake manifold with a starting device. With this method, better conditions for mixing the starter fluid with air are provided and the possibility of accompanying the first crankshaft rpm with additional fluid feed is afforded.

One of the starting accessory designs was developed in the NAMI [17]. The accessory consists of a double-action manual air pump, a mixer-emulsifier, and piping with sprayers (Fig. 133). The air pump is installed in the driver's cab, and the emulsifier is placed under the foot of the engine compartment near the engine. The starting fluid is poured into the emulsifier, the driver feeds air into the emulsifier from his cab, and the mixture of starting fluid with air that forms as an emulsion moves along the lines to the sprayers mounted in the intake manifold. The number of sprayers depends on the engine liter capacity and the shape of the intake manifold.

Two models of starting accessories are produced -- the 5PP-40 and the 6PP-40. They differ in mixer size, number of emulsion channels, and number of sprayers. However, both accessories are suitable for introducing starting fluid in either diesel or carburetor engines.

The main advantage of NAMI starting accessories is that owing to the multi-channel design the nonuniform distribution of starting emulsion in individual cylinders is obviated. The separated compressed air source and the emulsifier make it possible to locate the latter in direct proximity to the engine. This completely prevents emulsion condensing in the lines and ether vapor penetrating into the driver's cab [14].

Table 94. Limiting starting temperatures for the ZIL-375 engine using various oils

1 Масло	2 Температура пуска, °C	3 Состояние аккумуляторных батарей	Время пуска до начала устойчивой работы двигателя, сек 4
АС-8 5	—15	Холодные 9	15,0 *
АС-8 5	—26	»	1,8 **
АСЗп-10 6	—30	»	7,0 **
АСЗп-6 7	—35	»	4,5 **
АКЗп-6 8	—35	»	7,5 **
АМО-1	—40	Теплые 10	2,5 **

---

* Without starting fluid

** With starting fluid

Key:
1 -- Oil
2 -- Starting temperature
3 -- Condition of storage batteries
4 -- Starting time before stable engine operation begins, seconds
5 -- AS-8
6 -- ASZp-10
7 -- ASZp-6
8 -- AKZp-6
9 -- Cold
10 -- Warm

Table 94 presents the results of testing Arktika starting fluid on a ZIL-375 engine, Table 95 -- on a ZIL-130 engine, and Table 96 -- on a GAZ-66 engine.

Starts are held to be successful if at a given temperature the engine starts in not more than three tries lasting 10 seconds each, with an interval of 1 minute between tries. A start is called reliable if it was carried out with cold storage batteries at the ambient air temperature, and a start is held to be possible if it was carried out using warm storage batteries. The data indicate that the maximum engine starting temperatures using Arktika starting fluid depend on the grade of oil and the condition of the storage batteries.

Reliable starting of ZIL-375 engines using starting fluid can be achieved with AS-8 oil at temperatures down to -25° C; using ASZp-10 oil ---down to -30° C; and using AKCp-6 oil -- down to -35° C. The ZIL-130

Table 95. Starting time of ZIL-130 engine using ASZp-6 and "Arktika" starting fluid at different temperatures and cranking speeds of crankshaft

Температура пуска, °C 1	n, об/мин 2	Число попыток 3	4 Время, сек	
			до первой вспышки 5	до начала устойчивой работы 6
—20	18	1	2,6	3,2
—34	27	1	2,8	5,0
—34	20	2	12,1	18,1
—35	19	3	13,2	26,0
—40	25	3	13,0	25,6

Key: 1 -- Starting temperature
2 -- m, rpm
3 -- Number of tries
4 -- Time, seconds
5 -- before first firing
6 -- before beginning of stable operation

engine using ASZp-6 oil starts reliably when Arktika starting fluid is used at temperatures as low as -35° C. A reliable start was achieved for the GAZ-66 engine only down to a temperature of -28° C. This fact indicates the necessity of design improvements in the starting qualities of GAZ-66 engines.

It was of interest to rate the efficiency of Arktika starting fluid by the minimum engine rpm. Fig. 134 shows the temperature dependence of the starting rpm of a ZIL-130 engine when winter gasoline and northern gasoline were used, and when the starting fluid was used together with winter gasoline. Below the rpm which are delimited by the curves the engine does not start even after three tries of 10 seconds each. The relative efficiency of the starting increases with decrease in the starting temperature. The starting fluid is best used at temperatures of -25° C and below. The amount of fluid used per try is 10-40 ml.

It must be noted that in several cases, when starting fluids were tested, individual firings in cylinders were detected even at lower temperatures, however the engine did not develop revolutions. As shown by G. S. Savel'yev, at low temperatures the moment of resistance of the frictional forces is so large that it exceeds the indicated moment and the engine cannot switch into the independent-operating regime. When initial firings occur, the combustion of the mixture is severely drawn out and is characterized by low gas pressures. The maximum combustion pressure is achieved for a crank angle of 50-60° beyond the TDC and does not exceed 20 kg/cm^2 in magnitude.

Table 96. Limiting starting temperatures of GAZ-66 engine for different oils and gasolines (Arktika starting fluid was used)

Бензин (масло) 1	Состояние аккумуляторных батарей и степень их заряда 2	Предельная температура пуска, °С 3
Зимний (АС-8) 4	8 Холодные, 75%	−15
	9 Теплые, 100%	−20
Северный (АС-8) 5	8 Холодные, 75%	−18
	9 Теплые, 100%	−21
Зимний (АСЗп-6) 6	8 Холодные, 75%	−20
	9 Теплые, 100%	−26
Северный (АСЗ-6) 7	8 Холодные, 75%	−26
	9 Теплые, 100%	32
	8 Холодные, 75%	−28
	9 Теплые, 100%	−40

---

* Without starting fluid

** With starting fluid

Key:
1 -- Gasoline (oil)
2 -- Condition of storage batteries and degree of their charge
3 -- Limiting starting temperature
4 -- Winter (AS-8)
5 -- Northern (AS-8)
6 -- Winter (ASZp-6)
7 -- Northern (ASZ-6)
8 -- Cold
9 -- Warm

Further possiblities of improving cold starts of carburetor engines are associated with a reduction in the moment of resistance of frictional forces, mainly by reducing the viscosity of oils at low temperatures, and these possibilities are also associated with a large rise in the indicated moment in the starting period. Increases in the indicated moment during starting can be achieved by increasing the heat of combustion of the starting fluid. The lower heat of combustion of Arktika starting fluid is 9820 kcal/kg, that is, 5 percent less than for gasoline. A further rise in the heat of combustion of the mixture is possible only by incorporating compounds with higher heats of combustion in the starting fluids.

Starting fluids and engine wear. In the technical literature the view is widely held that the starting of a cold engine causes major wear in the cylinder-piston group and bearings. Studies conducted in recent years showed that wear occurring when diesel engines are started are not very high. Obviously, the increase in the wear resistance of the materials used and an upgrading in lubricating oils played a role in reducing starting wear.

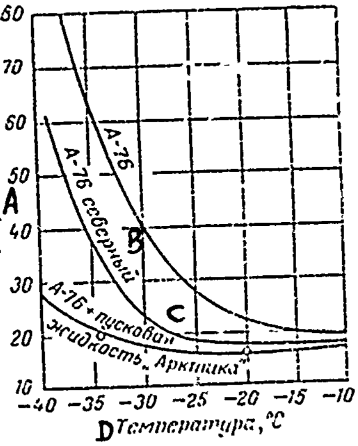

Fig. 134. Temperature function of the minimum starting rpm of the crankshaft of the ZIL-130 engine

Key: A -- m, rpm
B -- Northern A-76 gasoline
C -- A-76 gasoline + starting fluid, "Arktika"
D -- Temperature

The effect of starting cold carburetor engines on the wear of parts was investigated [15] in the cooling chamber in three ZIL-375 engines. The 5PP-40 starting device was installed on one and it was started with the starting fluid. The second engine was equipped with a P-100 series-built starting heater ensuring heating of the antifreeze in the cooling jacket up to 80-90° C, and heating of the oil in the sump to 50-60° C in 15-20 minutes of operation. The third engine had no special devices to facilitate starting, however its carburetor, just as in the other two engines, had the optimal starting tuning [19]. All three engines were started at -25° C 100 times each, and the starting temperature was selected so as to make comparative tests of the three methods of starting; below -25° C the ZIL-375 engine without starting-facilitating devices using selected samples of gasoline and oil failed to start. After each start the engine was warmed for 15 minutes in idle at 1200 rpm. The oil was replaced every 10 starts. The wear was determined by micrometer measurement of parts and by the cut-out crescent method (artificial reference lines).

The test results are shown in Table 97 and in Fig. 135.

The highest starting reliability (94 percent from the first try) was recorded for the engine in which starting fluid was used. The starting time was 2-2.5 times longer, when no facilitating devices were used, than when starting fluid and heater were used.

Table 97. Results of starting tests of three ZIL-375 engines using ASZp-10 oil (100 starts were made) [18]

Показатель 1	С пусковой жидкостью 2	С подогревателем П-100 3	Без средств облегчения пуска 4
Средняя продолжительность пуска, *сек* 5	5,1	6,6	13,9
Число удавшихся пусков 6			
с первой попытки 7	94	89	45
со второй попытки 8	5	9	33
с третьей попытки 9	1	2	22
Износ по микрометрическому обмеру (в *мм*) при расстоянии от верхней плоскости блока 10			
11 *мм*	0,010	0,014	0,016
15 »	0,019	0,019	0,018
22 »	0,016	0,014	0,025
42 »	0,014	0,012	0,020
67 »	0,011	0,010	0,022
97 »	0,011	0,008	0,022
107 »	0,009	0,007	0,022
115 »	0,009	0,008	0,022
132 »	0,009	0,006	0,021
Средний максимальный износ (метод вырезанных лунок), *мк* 11	10,0	8,0	12,0

Key:
1 -- Indicator
2 -- Containing starting fluid
3 -- Containing P-100 heater
4 -- Without starting facilitation
5 -- Mean starting time, seconds
6 -- Number of successful starts
7 -- from first try
8 -- from second try
9 -- from third try
10 -- Wear based on micrometer measurement (in mm) with the distance from the upper plane of the block as indicated below
11 -- Mean maximum wear (method of cut-out crescents), microns

It is clear from the micrometer measurement data that the wear in the cylinder liners of engines started with starting fluid and heater is roughly the same. The greatest engine wear is observed in the upper zone lying at a distance of 15-22 mm from the joint plane of the cylinder block. In absolute value, the maximum diametral wear of liners was 19 microns for these engines. In the case of the engine which was started without facilitating devices, the nature of the liner wear differed somewhat from that observed in the two other engines (cf. Table 97). The maximum wear amounted to 25 microns and varied virtually very little along the entire height of the power stroke of the piston rings.

Results of a more exact determination of cylinder liner wear by the cut-out crescent method showed that the changes in the liner wear heightwise (cf. Fig. 135) is approximately the same for all three engines and did not

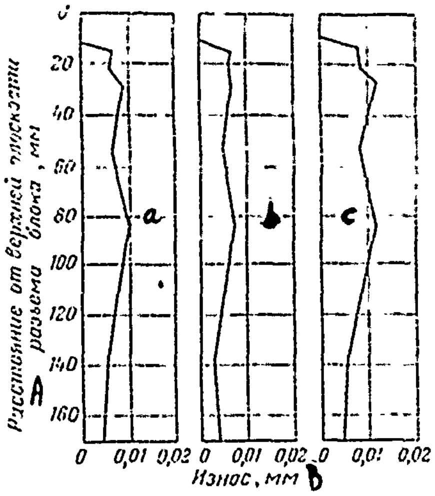

Fig. 135. Wear of cylinder liners of three engines (a, b, and c, respectively) found by the method of cut-out crescents
Key: A — Distance from upper plane of block joint
B — Wear

differ from the ordinary operating wear. The mean data on the maximum wear in cylinder liners based on the cut-out crescent method proved to be very close for all three engines, a very small and absolute value. Some increase in the wear recorded for the engine provided with no starting gas facilitating devices is evidently accounted for by the fact that several starts succeeded only from the second and third tries and the unburned gasoline swept the oil from the cylinder walls.

Micrometer measurement of the remaining engine parts showed that the wear in piston rings and grooves, bosses, pistons, upper connecting rod heads, crankshaft journals, push rods, and valve stems is negligible and lies within the limits of measurement precision. The clearances in the naked parts after the tests are within the limits stipulated by the drawings for new engines. Thus, it was established that engine part wear, for starting using Arktika starting fluid, is very low, represents a small fraction of total operating wear, and virtually differs little from the wear resulting by starting an engine using a heater.

The broad introduction of Arktika starting fluid will make it possible to significantly facilitate engine starting during winter, shorten the time required to prepare vehicles for operation, and thus increase the efficiency of automotive transportation.

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[To Chapter Nine]

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CHAPTER TEN

STORAGE, TRANSPORTING, AND SEVERAL ASPECTS OF THE USE OF GASOLINES

Changes in gasoline quality in storage and transporting

In transporting and storage, changes occur in the physicochemical properties of automotive gasolines, which ultimately leads to a deterioration in their operating qualities. These changes can be provisionally divided into three main groups:

changes associated with chemical processes occurring in the gasoline;

changes which derive from the evaporation of low-boiling hydrocarbons; and

changes caused by the appearance in fuel of foreign products (watering, incursion of mechanical impurities, etc.).

The deterioration in the operating qualities of automotive gasolines when they are stored or in transportation occurs first of all due to the chemical changes in gasolines on exposure to air oxygen.

In an earlier section of the book the chemical stability of automotive gasolines was discussed in close detail; it depends on the composition of the gasoline, the addition of anti-oxidants, etc. However, the stability of gasoline in storage in actual conditions can differ widely from the stability determined in laboratory conditions since the conditions themselves strongly affect stability.

Automotive gasolines are produced by refineries as a rule with some reserve of properties, and for a number of indicators that change most appreciably during storage, this quality reserve is specifically stipulated by the specifications on the automotive gasolines. For example, GOST 2084-67 specifies the norm for the existent gum content in gasoline at the production site when it is being delivered (7 mg/100 ml -- for A-66 gasoline, and 5 mg/100 ml -- for all other grades) and a higher norm -- at the gasoline consumption site (15 mg/100 ml -- for A-66 gasoline, and 10 mg/100 ml -- for A-72 and A-76 gasolines, and 7 mg/100 ml for AI-93 and AI-98 gasolines).

The reserve provided in the quality of gasolines based on the main variable indicators and the rate of change for these indicators determines the allowable storage time for automotive gasolines. Let us examine changes in the main indicators associated with chemical transformations of gasoline components.

The knock resistance of automotive gasolines in storage as a rule changes little. On prolonged storage, a drop in the octane number of 1-2 points is observed. This decrease is due to the formation of peroxide compounds in the gasoline. In spite of small changes in the octane number, upon storage gasoline may prove unsuitable quite often with respect to this indicator, since automotive gasolines are produced from refineries generally without a quality reserve with respect to knock resistance.

Primarily, the decrease in knock resistance in ethyl gasoline occurs owing to the decomposition of tetraethyl lead (cf. above). However, modern domestic ethyl automotive gasolines usually contain an anti-oxidant and the decomposition of tetraethyl lead in them is observed quite infrequently.

The existent gum content in automotive gasolines changes most rapidly and it is precisely this indicator that usually dictates the allowable storage time. The specified norms for the existent gum content at the production site and at the consumption site differ for gasolines of different grades and depend on their stabilities.

A-66 gasoline contains a high content of compounds that are oxidation-prone, has the lowest induction period for oxidation, and therefore the highest norms for the existent gum content are specified for this gasoline -- -- 7 mg/100 ml at the production site and 15 mg/100 ml at the consumption site. It must be noted that even the difference in the norms between the value at the consumption site and at the production site is also the largest for this gasoline -- 8 mg/100 ml, which is accounted for by the lower chemical stability of A-66 gasoline compared with other grades (this difference is 5 mg/100 ml for A-72 and A-76 gasolines, and 2 mg/100 ml for AR-93 and AR-98 gasolines).

In addition to the rise in the existent gum content in gasoline, acidity begins to increase. However, its maximum value (3 mg KOH/100 ml) is attained usually after the gasoline becomes unsuitable due to the existent gum content.

Chemical changes in gasolines cause a decrease in the oxidation induction period. However, this indicator is standardized only at the production site and its change with time is slight. A decrease in the oxidation induction period is observed when automotive gasolines undergo frequent pumping from one vessel to another.

It must be noted that a rise in the existent gum content in gasoline occurs independently of the oxidation induction period. The existent gums may accumulate above the allowable norms in a gasoline with a fairly high induction period.

Chemical changes in storage and transporting have practically no effect on all the other indicators of automotive gasoline quality.

The rate of chemical changes in storage and transportation of gasolines depends on temperature, contact of nonferrous metals with the gasoline, extent of container filling, number of repumpings, etc. [1]. The storage temperature has the most accelerating effect. A rise in the temperature of gasoline during storage is accompanied by accelerated oxidation and gum formation. Studies showed that when the storage temperature is increased 10° C, the rate of gum formation rises by 2.4-2.8 times.

The storage temperature of gasoline depends on the climatic zone, time of the year, capacity, and location of the storage vessel (above-ground, semi-underground, and underground) and on several other factors.

Gum formation in gasolines always occurs faster during the summer in the southern parts of the country. Automotive gasolines are stored best in semi-underground and underground storage tanks. Even on the hottest days the temperature of gasoline in these storage tanks remains significantly below the ambient air temperature.

When gasoline is stored in above-ground storage tanks, its temperature depends on the storage capacity of the vessel and on its paint coating. Above-ground storage tanks of low capacity, subjected to sunlight, heat up faster than large vessels; the mean temperature of gasoline in them is usually higher and gum formation proceeds faster.

To lower the gasoline temperature, above-ground storage tanks are painted white. Gum formation proceeds much slower in this kind of storage tank. Studies showed that all of the most common metals, in contact with gasoline, accelerated oxidation and the formation of gums. Copper and its alloys have the greatest accelerating action. Therefore when gasoline is stored in vehicle tanks where it is in contact with the brass inlet pipe and the brass filter mesh, gum formation proceeds faster than in drums of the same capacity.

The nature of the interior coating of fuel tanks strongly affects the rate of gum formation in gasoline. A zinc coating of the interior surface of a tank accelerates gum formation. This is also promoted by access of air oxygen to the gasoline surface. Gasoline is oxidized much slower in a hermetically closed container.

When gasoline is stored in a partially filled container, a large surface area of gasoline contact with air results, per unit of gasoline mass, and this thereby ensures the freer access of oxygen to the gasoline, and thus gum formation is accelerated.

Repeated repumpings of gasoline from container to container promote a decrease in chemical stability. In being repumped, automotive gasolines become saturated with air oxygen, the intensity of oxidation processes in it rises, and gum formation is accelerated.

Oxidation and gum formation in automotive gasolines is considerably accelerated when the gasolines are stored in the presence of gums or residues of gum-containing gasoline from a previous storage that have settled in the vessel.

Physical changes in gasolines during storage are associated with the evaporation of low-boiling components. The evaporation of light hydrocarbons leads to a rise in the density of gasolines and a deterioration in their starting qualities. Sealing of a container not only prevents chemical changes in gasoline, but also reduces the evaporation of low-boiling gasoline fractions. In gasolines produced on the basis of the straight-run and thermal cracking products, low-boiling fractions have the highest antiknock properties, therefore when their loss occurs the octane numbers of these gasolines decreases somewhat.

When ethyl automotive gasolines containing R-9 ethyl fluid are stored (most domestic gasolines contain precisely this fluid), in addition to the low-boiling fractions a volatile scavenger — ethyl bromide (boiling point 38° C) also evaporates. After storage, in the gasoline there may remain an amount of ethyl bromide which is insufficient to combine with all of the lead and carry it from the combustion chambers. When this gasoline is used in an engine, deposit formation can rise sharply.

Based on the results of experimental storage of automotive gasolines in different kinds of containers in different climatic zones, the following allowable storage times have been established (in months):

	Northern zone	Central zone	Southern zone
In above-ground storage tanks	30	24	12
In semi-buried and buried storage tanks	36	30	18
In drums	24	12	6
In above-ground storage tanks higher than 5000 meters*			
A-66 gasoline	18	18	6**
A-72 and A-76 gasolines	30	30	15

[display continued on following page]

	Northern zone	Central zone	Southern zone
In buried storage tanks*	36	36	24
In vehicle tanks	6	6/3***	3

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* Departmental periods.

** In storage tanks with gas-leveling system the storage period can be 18 months.

*** 6 months is the storage time in the fall-winter period, 3 months--in the spring-summer period.

In ordinary storage conditions, only those chemical changes which do not lead to the loss of gasoline overall quality can occur over the allowable storage time.

If automotive gasolines for some reason become unfit, their quality can be restored. The main method of restoration is to blend this gasoline with fresh gasoline with a quality reserve. By blending gasolines, one can improve indicators such as the fractional composition, octane number, gum content, and acidity.

In selecting the ratio of amounts of gasolines to be used in blending, one must select an excess of the better gasoline, since the fractional composition of the blend of the two gasolines is not an arithmetic mean of the fractional compositions of the gasolines used in the blending.

The antiknock properties of an automotive gasoline can be rectified by blending it either with a high-octane component or with a gasoline of a higher grade with a higher octane number, since automotive gasolines produced by refineries as a rule do not have a quality reserve for this indicator.

In calculations of the ratio of gasolines needed for blending, to some approximation it can be assumed that the octane number of the blend is the arithmetic mean between the octane number of the gasolines used in the blending. When benzene is added to the gasolines, one must remember that the blended octane number is higher than for benzene than in the true form.

Recovery of the antiknock properties of automotive gasolines by adding ethyl fluid can be achieved only at warehouses and depots that have special mixing equipment. Ethylation and supplementary ethylation of automotive gasolines without observing safety rules is categorically forbidden.

If the octane number of a gasoline decreases owing to the decomposition of tetraethyl lead, before recovery the gasoline must be carefully filtered to separate it from the precipitate of the lead compounds. The precipitate of the lead compounds may have no effect on the antiknock properties of ethyl gasoline. In this event, filtering the gasoline is sufficient to restore required quality. Filtered gasoline must be consumed as rapidly as possible, since the process of tetraethyl lead decomposition that has begun will continue even after filtration.

Recovery of automotive gasoline qualities such as the existent gum content and acidity can be achieved only by blending these gasolines with fresh gasolines, usually having a higher quality reserve with respect to these indicators. The gum content and the acidity of the gasoline blend is the arithmetic mean of these indicators of the gasolines used in the blending. Gasolines with restored existent gum content must be used first, since,the process of oxidation that has begun rapidly leads to the accumulation of new gum compounds.

To calculate the amount of the fresh gasoline required to recover the quality of another gasoline for any indicator that obeys the law of proportionality (gum content, acid and octane numbers), one can use the following formula:

$$K = \frac{p_3 - p_2}{p_1 - p_2} \cdot 100$$

where K is the amount of better-quality gasoline required to rectify the poorer-quality gasoline, percent; p_1 is the value of the rectified physicochemical indicator of the better gasoline; p_2 is the value of the rectified physicochemical indicator of the poorer gasoline; and p_3 is the value of the physicochemical indicator of the mixture that must be obtained after rectification.

One must note that to restore the properties of a gasoline directly for a number of indicators, it is necessary to calculate for each indicator separately and to take the largest amount of gasoline obtained in the calculations for the blending step.

Restoration of the quality of an automotive gasoline with respect for its content of mechanical impurities can be achieved by settling, followed by filtration. Choice of the filter depends mainly on the amount of gasoline to be rectified. It is convenient to use fuel-charging filters and special removal filters for fuels.

Watered nonethyl automotives gasolines can be used for direct purposes after settling and decanting of the aqueous layer. Ethyl automotive gasolines, after intense dewatering, must be verified in the laboratory for their scavenger content and only thereupon can one solve the problem as to their use. When there is slight watering of ethyl gasolines, they can be used in a blend with other ethyl gasolines not subjected to watering.

Losses

The delivery of automotive gasolines from petroleum refineries to consumption sites involves significant losses. The main component of all gasoline losses are those due to evaporation.period occurs in storage, pouring, filling, transporting, and filling of vehicles, and also when during use the gasoline evaporates from fuel tanks, carburetors, etc. Evaporation losses occur for the following main reasons: mechanical displacement of vapor by filled gasoline, thermal expansion of the vapor and liquid phases, reduction in atmospheric pressure, saturation (or final saturation) of the vapor space by the gasoline vapors, sweeping of vapors by wind through cracks, gaseous siphoning, and vapor diffusion [2]. The relative importance of each of these kinds of losses in the overall loss balance differs and depends on numerous factors, however, as shown by experiments, the main losses in storage are associated with the final saturation of the vapor space and thermal expansion of the air-vapor mixture for so-called small "respirations" caused by the diurnal temperature change.

The paramount factor affecting gasoline losses in various operations is gasoline volatility. However, the volatility of gasolines in storage is only indirectly associated with indicators such as saturated vapor pressure, boiling-onset temperature, 10 percent gasoline distillation, etc. None of these indicators directly determines the tendency of automotive gasolines to undergo losses in storage and transportation, although the latter does depend on all these indicators.

I. P. Budarov [2] developed a direct method for estimating the tendency of gasolines to undergo evaporation losses, which was adopted as the standard procedure (GOST-6368-52). Essentially the method consists in determining the excess gasoline mass (in percent by weight) after it has been purged by a strictly specific volume of air. In control tests, 10 ml of gasoline is used and it is swept with a ten-fold volume of air 20° C in a special instrument. There is a relationship between the tendency of gasolines to undergo evaporation losses and the mean-annual losses in storage in various climatic zones (Fig. 136).

Study of the tendency of automotive gasolines to suffer evaporation losses takes on special urgency at the present time due to the fact that the petroleum refining industry has begun to produce the winter grade of gasolines with the saturated vapor pressure up to 700 mm Hg. Various low-boiling components can be used in preparing winter and arctic gasolines -- -- butane, natural gasoline, isopentane, etc. The amount and quality of the low-boiling components incorporated in a gasoline are also reflected in the tendency of commercial gasolines to suffer evaporation losses.

An estimate was made of the evaporation loss tendency of thermal cracking gasoline and platforming gasoline by the above-described I. P. Budarov method, when different amounts of butane, natural gasoline, and isopentane was added to them (Table 98).

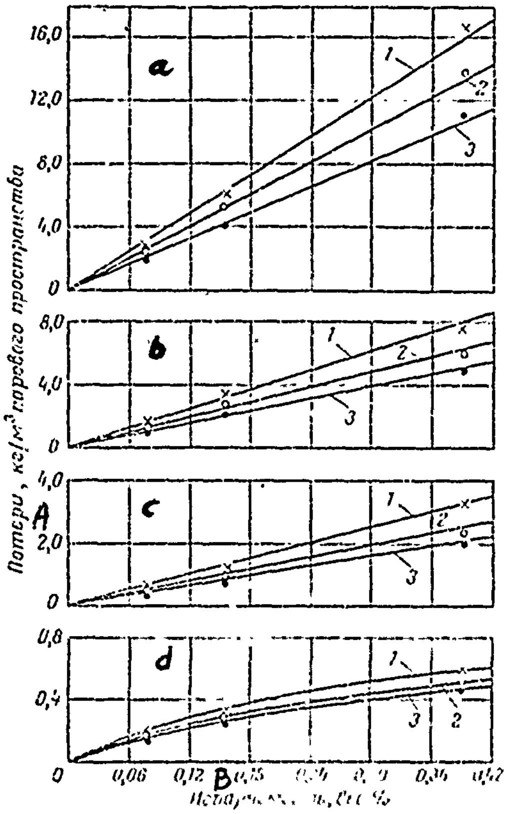


Fig. 136. Dependence of mean-annual gasoline losses in 1 month storage in above-ground horizontal (a) and vertical (b), semiunderground (c) and underground (d) tanks on gasoline volatility (GOST-6963-52):
1 -- Southern zone; 2 -- Central zone; 3 -- Northern zone
Key: A -- Losses, kg/m^3 of vapor space
B -- Volatility, percent by weight

The results indicate that the addition of butane does not lead to an appreciable rise in evaporation losses. When 10 percent butane was added, the evaporation losses increased by about the same amount as upon the addition of 15 percent natural gasoline or isopentane.

M. B. Vol'f et al. observed changes in the saturated vapor pressure of blends of A-72 gasoline with butanes (butane content of 4.2 and 8.3 percent) when stored in bottles fitted with capillaries. The results show that the stability of butane-containing gasolines is particularly high: after 3 months' storage at 23-25° C, the vapor pressure dropped by 60 mm, and after 3 months' storage at 5-7° C -- by 30-40 mm Hg. When stored at lower temperatures in the northern regions of the country, the drop in the saturated vapor pressure will be even less.

Table 98. Gasoline losses from evapcration; estimate based on the I. P. Budarov method [2]

Бензин 1	$P_н$, мм рт. ст. 2	Среднегодовые потери за 1 месяц хранения, кг на 1 м³ парового пространства 3					
		Северная зона 4			Средняя зона 5		
		наземный резервуар 6	полуподземный резервуар 7	подземный резервуар 8	наземный резервуар 6	полуподземный резервуар 7	подземный резервуар 8
Бензин термического крекинга 9	360	1,8	0,7	0,2	2,2	0,9	0,3
с 3% бутана 10	490	2,9	1,2	0,3	3,6	1,4	0,4
с 7% бутана 11	590	4,0	1,6	0,4	4,9	2,0	0,4
с 10% бутана 12	645	4,5	1,9	0,4	5,6	2,4	0,5
с 5% газового бензина 13	500	2,7	1,1	0,3	3,2	1,3	0,3
с 10% газового бензина 14	590	3,4	1,4	0,4	4,3	1,7	0,4
с 15% газового бензина 15	630	4,4	1,8	0,4	5,5	2,2	0,5
с 5% изопентана 16	475	2,2	0,9	0,3	3,0	1,1	0,3
с 10% изопентана 17	555	2,9	1,2	0,3	3,9	1,4	0,4
с 15% изопентана 18	600	3,9	1,6	0,4	5,0	2,0	0,4
Бензин платформинга 19	560	3,3	1,3	0,3	4,2	1,6	0,4
с 3% бутана 10	630	4,4	1,8	0,4	5,5	2,2	0,5
с 7% бутана 11	690	5,0	2,1	0,5	6,3	2,5	0,5
с 10% бутана 12	715	6,5	2,5	0,5	8,0	3,1	0,6
с 5% газового бензина 13	625	4,4	1,8	0,4	5,5	2,2	0,5
с 10% газового бензина 14	660	5,5	2,2	0,5	6,7	2,7	0,5
с 15% газового бензина 15	675	6,3	2,4	0,5	7,9	3,0	0,6
с 5% изопентана 16	600	4,5	1,9	0,4	5,6	2,4	0,5
с 10% изопентана 17	630	5,5	2,2	0,5	6,7	2,7	0,5
с 15% изопентана 18	650	6,0	2,4	0,5	7,3	2,9	0,5
Товарный бензин 20							
летний 21	500	3,0	1,3	0,3	3,7	1,5	0,4
зимний 22	650	4,9	2,0	0,4	6,0	2,1	0,5
»	615	4,3	1,7	0,4	5,4	2,1	0,5

Key:
1 -- Gasoline
2 -- P_{sat}, mm Hg
3 -- Mean-annual losses in 1 month storage, kg per m³ of vapor space
4 -- Northern zone
5 -- Central zone
6 -- above-ground tank
7 -- semiunderground tank
8 -- underground tank
9 -- Thermal cracking gasoline
10 -- with 3 percent butane
11 -- with 7 percent butane
12 -- with 10 percent butane
13 -- with 5 percent natural gasoline
14 -- with 10 percent natural gasoline
15 -- with 15 percent natural gasoline
16 -- with 5 percent isopentane
17 -- with 10 percent isopentane
18 -- with 15 percent isopentane
19 -- Platforming gasoline
20 -- Commercial gasoline
21 -- summer
22 -- winter

Table 99. Loss norms for automotive gasolines (3, 4)

Виды потерь 1	Южная зона 2		Средняя зона 3		Северная зона 24	
	осенне-зимний период 4	весенне-летний период 5	осенне-зимний период 4	весенне-летний период 5	осенне-зимний период 4	весенне-летний период 5
При хранении в резервуарных емкостях (в кг/м^2 поверхности испарения в месяц) 6						
резервуары наземные металлические с понтонами 7	0,2516	0,9000	0,1160	0,6188	0,0902	0,4490
» заглубленные железобетонные 8	0,2800	0,5000	0,1290	0,4140	0,1000	0,3750
» наземные металлические емкостью 2000 м^3 и более 9	1,0050	3,600	0,4600	2,4800	0,3630	1,8000
» » металлические емкостью 1000 м^3 и менее 10	1,2580	4,5000	0,5800	3,0940	0,4510	2,2450
При отпуске в резервуары, нефтеналивные суда, цистерны и мелкую тару, % от отпущенного количества 11						
в резервуары наземные металлические с понтонами 12	0,0068	0,0100	0,0052	0,0088	0,0042	0,0078
» » заглубленные железобетонные 13	0,0149	0,0213	0,0106	0,0170	0,0085	0,0136
» » наземные металлические 14	0,0340	0,0500	0,0250	0,0400	0,0200	0,0320
» баржи и танкеры 15	0,0326	0,0590	0,0236	0,0475	0,0191	0,0397
» цистерны железнодорожные 16	0,0271	0,0604	0,0208	0,0487	0,0168	0,0420
» автоцистерны, мерники, бочки, бидоны, баки машин 17	0,1130	0,1590	0,0553	0,0993	0,0373	0,0753
При приеме из резервуаров, нефтеналивных судов, цистерн и автоцистерн, % от принятого количества 18						
из резервуаров в резервуары наземные металлические, заглубленные и железобетонные 19	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000
из барж и танкеров 20						
в наземные металлические резервуары с понтонами 21	0.0105	0,0150	0,0075	0,0120	0,0060	0,0096
» заглубленные железобетонные резервуары 22	0,0149	0,0213	0,0106	0,0170	0,0085	0,0136
» наземные металлические резервуары 23	0,0350	0,0500	0,0250	0,0400	0,0200	0,0320

Table 99 [Conclusion]

Виды потерь 1	Южная зона 2		Средняя зона 3		Северная зона 24	
	осенне-зимний период 4	весенне-летний период 5	осенне-зимний период 4	весенне-летний период 5	осенне-зимний период 4	весенне-летний период 5
из железнодорожных цистерн 25						
в наземные металлические резервуары с понтонами 26	0,0122	0,0171	0,0096	0,0138	0,0078	0,0114
» заглубленные железобетонные резервуары 27	0,0184	0,0240	0,0136	0,0196	0,0110	0,0162
» наземные металлические резервуары 28	0,0406	0,0570	0,0320	0,0460	0,0260	0,0380
из автоцистерн 29						
в наземные металлические резервуары с понтонами 30	0,0135	0,0180	0,0104	0,0144	0,0084	0,0120
» заглубленные железобетонные резервуары 31	0,0137	0,0250	0,0144	0,0202	0,0116	0,0168
» наземные металлические резервуары 32	0,0450	0,0600	0,0340	0,0480	0,0280	0,0400
В траншейных резервуарах с глубиной засыпки 35 см, поверхностью испарения 100 м² и высотой 7 м 33						
при приеме бензинов зимнего вида 34	0,0655	0,1345	0,0516	0,1068	0,0403	0,0905
при приеме бензинов летнего вида, % от принятого количества 35	0,0491	0,1009	0,0387	0,0801	0,0307	0,0679
при хранении бензинов зимнего вида 36	0,1569	0,3697	0,0625	0,2500	0,0412	0,1796
при хранении бензинов летнего вида, кг/м² поверхности в месяц 37	0,1180	0,2780	0,0470	0,1880	0,0310	0,1350
при отпуске бензинов зимнего вида 38	0,1460	0,2144	0,1007	0,1612	0,0735	0,1260
при отпуске бензинов летнего вида, % от отпущенного количества 39	0,1098	0,1612	0,0757	0,1212	0,0553	0,0947

Key:
1 — Kinds of losses
2 — Southern zone
3 — Central zone
4 — autumn-winter period
5 — spring-summer period
6 — When stored in storage tanks (in kg/m^2 of evaporation surface per month)
7 — above-ground metal storage tanks with pontoons
8 — buried reinforced-concrete storage tanks
9 — above-ground metal storage tanks 2000 m^3 and higher in capacity
10 — above-ground metal storage tanks 1000 m^3 and higher in capacity
11 — When released into storage tanks, oil tankers, tanks, and small containers, percent of released amount
12 — into above-ground metal storage tanks with pontoons
13 — into buried reinforced-concrete storage tanks
14 — into above-ground metal storage tanks
15 — into barges and tankers
16 — into rail car tanks
17 — into tank trucks, calibrated tanks, drums, carboys, and vehicle tanks
18 — When received from storage tanks, tankers, tanks, and tank trucks, percent of received amount
19 — from storage tanks into above-ground metal, buried, and reinforced-concrete storage tanks

[Key continued on following page]

[Continuation of Key to Table 99]

20 -- from barges and tankers
21 -- into above-ground metal storage tanks with pontoons
22 -- into buried reinforced concrete storage tanks
23 -- into above-ground metal storage tanks
24 -- Northern zone
25 -- from rail car tanks
26 -- into above-ground metal storage tanks with pontoons
27 -- into buried reinforced-concrete storage tanks
28 -- into above-ground metal storage tanks
29 -- from tank trucks
30 -- into above-ground metal storage tanks with pontoons
31 -- into buried reinforced-concrete storage tanks
32 -- into above-ground metal storage tanks
33 -- In trench storage tanks with 35 cm deep fill, evaporation surface 1000 m^2, and 7 m height
34 -- when receiving winter grade gasoline
35 -- when receiving summer grade gasolines, percent of received quantity
36 -- when storing winter grade gasoline
37 -- when storing summer grade gasolines, kg/m^2 of surface per month
38 -- when releasing winter grade gasolines
39 -- when releasing summer grade gasolines, percent of released amount

The same table, Table 98, presents data on the tendency of commercial automotive gasolines of winter grades to undergo evaporation losses. Storage of winter grade gasolines will be accompanied by losses that are 1.5 times greater than the losses for summer gasoline with a saturated vapor pressure of 500 mm Hg. It must be noted that all these data must be checked and refined in conditions of experimental storage. The norms for automotive losses currently in effect do not allow for their subdivision into winter and summer grades (Table 99). Only for operations in large trench storage tanks do the loss norms provide for a distinction between summer and winter gasolines.

In the departmental norms for automotive gasoline losses, a distinction is provided between losses suffered in prolonged storage and in constant consumption. Obviously, in specifying the norms for the natural losses in automotive gasolines, a great deal of work based on actual data lies ahead.

Contaminants

Composition of contaminants. In production, transportation, storage, and use mechanical impurities enter automotive gasolines; their particles are irregular in shape and not more than 60 mm in size. All large impurities settle out in gasoline under their own weight.

Particles smaller than 60 microns cannot be distinguished in gasoline with the unaided eye, therefore, the requirement in the standard that gasoline poured into a glass cylinder be clear is virtually always satisfied. In other words, the existing specifications on the quality of gasoline does not regulate the content of mechanical impurities [5-9].

Analysis of numerous tests of automotive gasoline sampled from tanks of various motor vehicles in different climatic and road conditions show that the contamination of gasolines fluctuates from 5 to 30 g/ton:

	Sampling time	Content of Mechanical Impurities, g/ton
Moscow	Winter	7.8
Moscow	Summer	16.3
Minsk	Winter	9.3
Minsk	Summer	15.9
Kazan'	Winter	21.6
Kazan'	Summer	39.6
Yevpatoriya	"	24.1
Krasnoyarsk	"	37.2
Altayskiy Kray	"	36.3
Golodnaya Steppe	"	283.1

The results of spectral determination of the elementary composition of mechanical impurities isolated from different gasolines (Table 100) makes it possible to establish the main sources of gasoline contamination.

Iron, copper, zinc, and several other metals enter into gasoline mainly as corrosion products of plant equipment, storage tanks, pipelines and fittings, feed system parts, and also due to the wear of pumping facilities. Silicon, aluminum, and other elements enter gasoline in the form of oxides with soil dust. Lead enters gasoline as the product of the decomposition of the antiknock — tetraethyl lead. Elements such as sodium, cobalt, and others can remain in gasoline due to its inadequate scrubbing after the alkali wash, partial entrainment of catalyst, etc.

Table 100. Ash content of contaminants in automotive gasolines and content of elements in ash fraction

Показатель 1	Образец 1 2	Образец 2 3	Образец 3 4	Образец 4 5
Зольность загрязнений, % 6	67,16	78,96	91,50	91,40
Содержание элементов, %, на зольную часть: 7				
Ba	0,1	0,20	Нет 8	0,03
Na	0,45	2,55	1,60	1,10
Ti	0,60	1,80	Нет 8	[illegible]
Al	1,30	2,24	19,69	11,71
Fe	44,50	32,00	37,95	[illegible]
Mg	0,60	1,11	0,72	2,74
Cu	4,50	5,50	0,20	0,01
Sn	11,50	5,55	0,10	Нет 8
Ni	0,05	0,10	0,08	Нет 8
Cr	Нет 8	0,15	Нет 8	0,02
Si	19,70	28,63	30,01	35,19
Zn	11,10	7,02	2,01	0,35
Mn	1,10	0,08	0,03	0,15
Pb	1,90	7,96	7,55	9,02
Co	0,06	Нет 8	Нет 8	Нет 8
Ca	1,90	4,81	4,81	[illegible]

Remark. P, K, V, Be, Sr, Cd, Ag, Mo, and Sb are the remainder.

Key:
1 -- Indicator
2 -- Sample 1
3 -- Sample 2
4 -- Sample 3
5 -- Sample 4
6 -- Ash content of contaminants
7 -- Content of elements, percent, for the ash fraction

Results of studies showed that the main and decisive source of contamination for automotive gasolines is atmospheric (soil) dust. It is precisely for this reason that the contamination of automotive gasolines is higher in summer than in winter.

The contamination of gasolines in vehicle tanks rises especially sharply for travel on village dirt roads. In domestic vehicles the fuel tank inlets as a rule are located at the locations of greatest air contamination. And the vents at the gas tank caps either are not put in place, or else do not function due to the lack of hermeticity of the caps.

Protection of gas tanks against the incursion of atmospheric dust by using a special air filter leads to an appreciable reduction in gasoline contamination:

Sampling location	Content of mechanical impurities, g/ton
From gasoline pump in the filling of a vehicle	12.30
From gasoline tank without filter, after a run of 5000 km	24.10
From vehicle tank with filter after a run of 5000 km	14.05

Effect of contaminants on engine performance. Mechanical impurities contained in gasoline can affect engine operation:

reduce reliability and longevity of the feed systems;

increase the wear in the rubbing parts of the engine; and

increase the amount of deposits in the intake system and the combustion chamber.

A large amount of material has been accumulated on the effect of mechanical impurities on the functioning of the feed system in carburetor engines and the main principles have been found [10-17]. It was established that mechanical impurities, on entering a carburetor, cause plugging of the channels and the jet nozzles. If the contaminants adhere to the working bevel of the float mechanism valve or of its seat, the valve ceases to maintain the required gasoline level in the float chamber. The incursion of contaminants under the back valve ball of the acceleration pump upset valve hermeticity, and as a result some of the gasoline returns to the float chamber at the instant of pump operation. This leads to deterioration of the engine response, and to the appearance of "pockets" when the engine crankshaft rpm is increased.

An increase in the wear on rubbing parts and the metering orifices of carburetors when gasolines with different levels of contamination are used has been noted. Mechanical impurities contained in gasolines upset the calibration of jet nozzles, increase their cross section, and distort the nature of gasoline flow.

It has been established that mechanical impurities in gasoline participate in forming deposits in the intake system and carbon deposits in the combustion chambers of the engine. And not only is the total amount of deposits increased, but their hardness and abrasiveness as well [17-20]. The participation of mechanical impurities of gasoline in forming deposits is indicated by the similarity of their elementary composition (in percent of ash content):

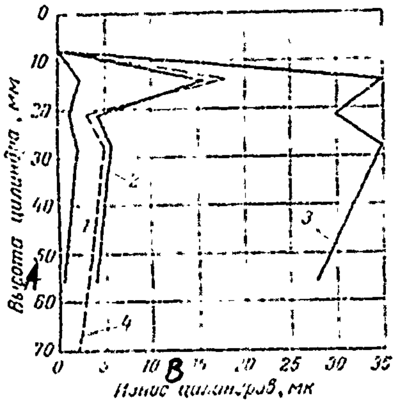


Fig. 137. Wear in ZIL-130 engine when operated on gasoline with different quartz sand content:
1 -- 0 g/ton; 2 -- 13.5 g/ton;
3 -- 40 g/ton; 4 -- Usual operating wear
Key: A -- Cylinder height, mm
B -- Cylinder wear, microns

	Impurities in gasoline	Deposits in intake manifold		Impurities in gasoline	Deposits in intake manifold
Na	1.60	1.43	Cr	None	0.03
Ti	None	0.27	Si	30.01	25.42
Al	13.69	10.01	Zn	2.01	2.10
Fe	37.95	39.60	Mn	0.03	0.34
Mg	0.72	3.64	Pb	7.96	5.46
Cu	0.20	2.04	Co	None	0.19
Sn	0.10	0.12	Ca	4.81	5.55
Ni	0.08	0.03			

Remark. Up to 100 percent of the remainder is accounted for by P, K, V, Be, Sr, Cd, Ag, Mo, and Sb.

The effect of mechanical impurities in gasoline on the wear of the cylinder-piston group has been established uniquely by recently conducted studies. Two ZIL-130 vehicles were tested in road conditions for operation on pure gasoline not containing mechanical impurities, and on the same grade of gasoline, but now contaminated with quartz dust (GOST 8002-62) in the amounts of 13.5 and 40 g/ton. The vehicles covered runs from 5000 to 7000 km with each pint of fuel. Results of rating cylinder wear by measurements of the lunes are shown in Fig. 137. The figure also presents data on the operating wear of this type of engine in ordinary conditions.

An increase in the concentration of mechanical impurities in gasoline increases the wear rate; the nature of wear due to mechanical impurities in gasoline is identical to ordinary operating wear.

Similar data were obtained in tests made of ZIL-130 engines in the area around Simseropol' [21].

Thus, mechanical impurities in gasoline participate in wear incurred by the cylinder-piston group of an engine and a reduction in the level of gasoline contamination permits higher engine longevity. Particles of mechanical impurities, depending on their size and abrasiveness properties, have different effects on engine wear. A considerable number of studies, whose results are represented in part in Fig. 138, have been published on the effect of particle size on engine wear.

In spite of the contradictory nature of these results, it must be assumed that all particles larger than 10 microns in size participate in the wear incurred by the cylinder-piston group.

The abrasiveness properties of mechanical impurities have been investigated to a lesser extent. Available data indicate that abrasive properties depend on particle size and differ apprecaibly for different samples of the same dust.

The abrasive properties of mechanical impurities contained in automotive gasolines depend on the service conditions, condition of the roads, etc.

The size of mechanical impurity particles contained in gasoline is more constant and some differences are mainly due to the operating season. Fig. 139 presents averaged data on the granulometric composition of mechanical impurities in samples of automotive gasolines taken in different parts of the USSR in different times of the year.

In domestic motor vehicles, filter compartments in the feed system are such that virtually all mechanical impurities enter an engine together with the gasoline.

The system of gasoline filtration in ZILp trucks contains two main filter compartments -- in the first-stage filter and the second-stage filter (Fig. 140). The first-stage filter has 50 micron slits between the plates and therefore admits all particles smaller than 50 microns in size; the second-stage filter consists of a metal screen with 140 micron mesh, therefore it admits all impurities.

Similar filters are used also in other models of domestic vehicles.

These data indicate the necessity of improving the filtration of gasolines in the feed systems of domestic vehicles, which can afford a

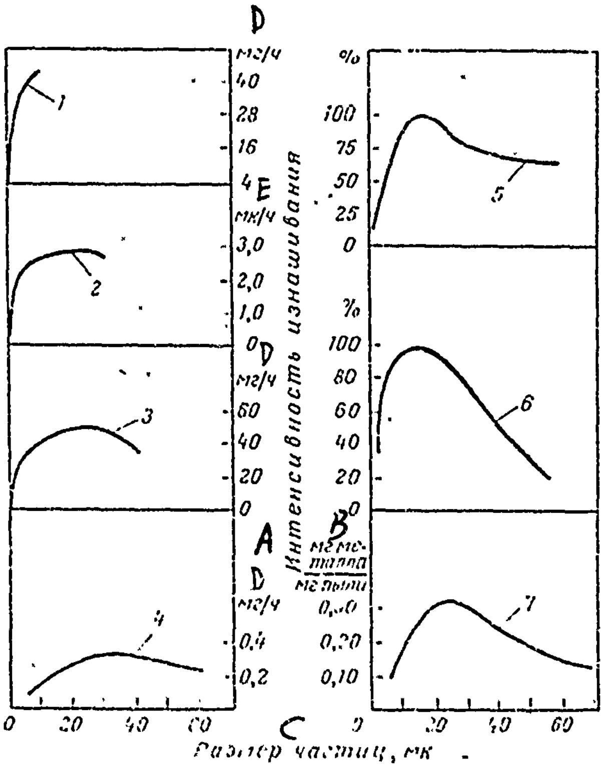


Fig. 138. Effect of contaminant particle size on wear rate:

1 -- Wear rate of ring according to V. Ye. Mayev [23, 24]

2, 3 -- Wear rate of upper section of cylinder and first ring according to N. F. Pochtarev [22]

4, 5 -- Wear rate according to A. I. Nisnevich [25]

6 -- Wear rate of MZMA-407 engine according to D. I. Vysotskiy [26]

7 -- Results of tests made by the American California Research Corporation [27]

Key: A -- Wear intensity
B -- mg of metal/mg of dust
C -- Particle size, microns
D -- mg/hr
E -- microns/hour

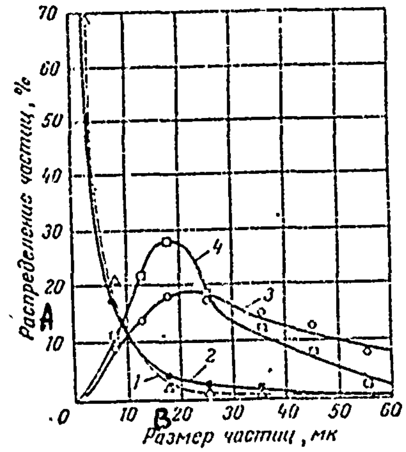


Fig. 139. Mechanical impurities in gasoline:
1 -- in winter, based on the number of particles
2 -- in summer, based on the number of particles
3 -- in summer, based on the volume of particles
4 -- in winter, based on the volume of particles
Key: A -- Particle distribution
B -- Particle size, microns

considerable increase in engine operating reliability and longevity. Calculations show that the first-stage filter must drop particles larger than 35 microns in size, and the second-stage filter -- particles larger than 10 microns. Then both filters will be roughly evenly loaded and their service times will be similar.

The fist-stage can evidently be left in the slit design, by reducing slit size down to 35 microns, while the second-stage filter must contain an effective filtering compartment with a trapping precision of 10 microns. The second stage filters consisting of nonfabric material, various kinds of paper, fluoroplastic, ceramic, cermet, and other types have been tested and proposed. They all have certain advantages and disadvantages. However, the trend now developing in our country toward increasing the longevity of domestic motor vehicles requires the most rapid introduction of an optimal system of purifying gasolines free of mechanical impurities.

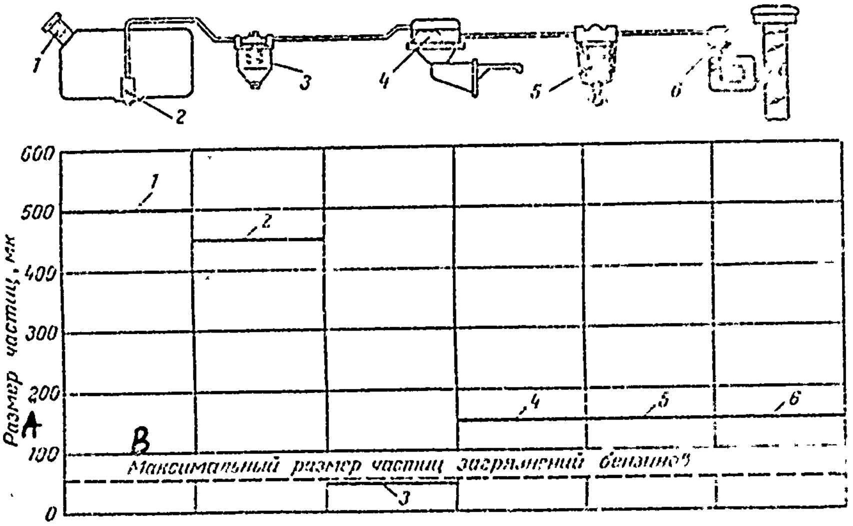


Fig. 140. Mesh size of filters in feed systems of domestic motor vehicles and maximum particle size of gasoline contaminants:

1 -- Gasoline tank inlet filter
2 -- Gasoline intake pipe filter
3 -- Main-line settling tank filter
4 -- Gasoline pump filter
5 -- Final-stage filter
6 -- Carburetor filter
Key: A -- Particle size, microns
B -- Maximum particle size of gasoline con- contaminants

Toxicity of gasolines and their combustion products

The problem of cleaning the air basin of large cities has been receiving close attention at the present time owing to the vigorous development of motor transportation [28-43]. It has been established that 50-90 percent of all harmful substances in the air over the largest cities of the world owe their origin to the motor vehicle. The concept "motor vehicle toxicity" has been introduced and is solidly entrenched, to which the toxicity of the substances released into the atmosphere in motor vehicle operation relates. We can single out three main ways of contaminating the atmosphere with toxic compounds. These include, first of all, exhaust gases, later -- crankcase gases entering the atmosphere in the ventilation of the crankcase, and, finally, the vapor of gasoline evaporating in the fuel system of an engine and fuel tank.

The main source of contamination of the atmosphere are the exhaust gases, in which about 200 different compounds have been found in the gaseous, liquid, and solid states. Some of these compounds are not only toxic, but also carcinogenic. The composition of exhaust gases (in percent by volume) of carburetor and (for comparison) diesel engines is given below:

	Carburetor engines	Diesel engines
N_2	74-77	76-78
O_2	0.3-8.0	2.0-18.0
H_2O (vapor)	3.0-5.5	0.5-4.0
CO_2	5.0-12.0	1.0-10.0
CO*	5.0-10.0	0.01-0.50
Oxides of nitrogen*	0.0-0.8	0.0002-0.5000
Hydrocarbons*	0.2-3.0	0.009-0.500
Aldehydes*	0.0-0.2	0.001-0.009
Carbon black *	0.0-0.4 (g/m^3)	0.01-1.10 (g/m^3)
Benzpyrene-3,4**	Up $10-20 \cdot 10^{-6}$ (g/m^3)	Up to $10 \cdot 10^{-6}$ (g/m^3)

---

* Toxic components
** Carcinogen

All toxic components of exhaust gases can be divided into several groups.

Carbon monoxide is a colorless gas, without odor, and lighter than air. It causes oxygen starvation in an organism and damage to the central nervous system. The carbon monoxide content in exhaust gases of gasoline engines is up to 10 percent, but not more than 0.5 percent in the gases of diesel engines.

The reason for the appearance of carbon monoxide is incomplete combustion, therefore, the carbon monoxide content in the exhaust gases of gasoline engines depends primarily on the excess air coefficient (Fig. 141). Owing to the nonuniformity of fuel distribution by charge mass, carbon monoxide is present in exhaust gases even when the air-to-fuel ratio is stoichiometric ($\alpha = 1$).

Oxides of nitrogen. Exhaust gases can contain nitrogen oxide (NO), nitrogen dioxide (NO_2), and the higher oxides (up to N_2O_5). On entering the human organism, they combine with water, forming compounds of nitric, nitrous, and other nitrogen-containing acids. Oxides of nitrogen are roughly

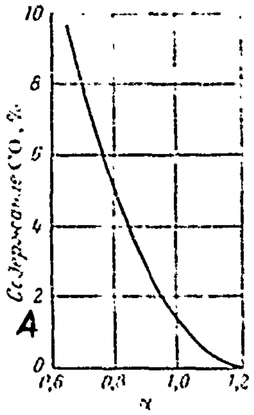


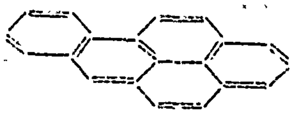
Fig. 141. Dependence of carbon monoxide content in exhaust gases [36] on mixture composition (GAZ-51 engine, crank speed 2200 rpm)
Key: A -- CO content

10 times more dangerous than carbon monoxide for man. The dependence of the amount of oxides of nitrogen on adjustable engine parameters is complex. When the composition of the mixture is varied, the amount of the oxides of nitrogen present in the exhaust gases has a maximum for $\alpha = 1.05$-1.10, and when the ignition advance is near-optimal, in terms of torque. With increase in compression rato and in the charge factor, the content of the oxides of nitrogen increases in exhaust gases.

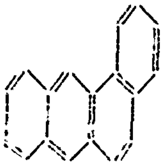
Aldehydes are represented in exhaust gases mainly by three compounds: formaldehyde, acrolein, and acetaldehyde. Aldehydes act as irritants to the mucosa and attack the central nervous system. The proportion of toxicity represented by the aldehydes does not exceed 4-5 percent of total exhaust gas toxicity.

Hydrocarbons are the most numerous groups of toxic compounds in exhaust gases. Representatives of all hydrocarbon classes have been detected: paraffins, naphthenes, olefins, diolefins, and aromatic hydrocarbons, including those with several condensed benzene rings. Hydrocarbons differ widely in toxic properties. However, until recently the question of hydrocarbon toxicity has not been adequately studied and standardizing their content in exhaust gases is being carried out on a total-content basis. It has been noted only that unsaturated hydrocarbons are oxidized in air owing to photochemical reactions in the presence of nitrogen dioxide, forming poisonous oxygen-containing compounds. These compounds participate actively in forming stable toxic fogs in the form of haze hanging over a city with intense vehicular traffic (smog). The battle against smog is a most urgent problem in several cities of the United States, Japan, Great Britain, etc.

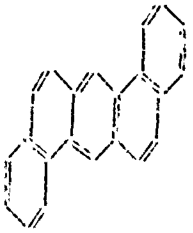
Carcinogenic compounds have been found in exhaust gases fairly recently. In the exhaust gases of gasoline engines the content of these compounds is especially significant. Carcinogenic compounds include condensed polycyclic aromatic hydrocarbons which cause cancer in animals. The best studied carcinogenic compound found in exhaust gases is 3,4-benzpyrene, which has the following structural formula:



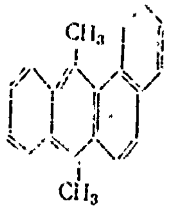
Carcinogenic compounds include derivatives of anthracene with the following structure, detected in exhaust gases but inadequately studied:



1,2-benzanthracene



1,2,6,7-dibenzanthracene



5,10-dimethyl-1,2-dibenzanthracene

The appearance in exhaust gases of polycyclic aromatic hydrocarbons is evidently associated with thermal decomposition and condensation of hydrocarbons in the combustion chamber in the preflame period. However, the mechanism of polyring aromatic hydrocarbon formation has not been clarified thus far.

Oxides of sulfur (when sulfur gasolines are used), or oxides of lead, bromine, chlorine, and their compounds (when ethyl gasolines are used) are present in exhaust gases.

The role of individual components in the total toxicity of exhaust gases differs and is determined mainly by the engine tuning, engine model, design features, technical condition, etc. All these questions have been studied quite closely and results of these studies have been published in the literature [29, 36-38].

The use of ethyl gasolines increases the toxicity of exhaust gases. In addition to lead, gas toxicity is increased by its halogen compounds. It is assumed [44] that aerosols of halogen compounds of lead can undergo catalytic and photochemical transformations, participating in smog formation. The possibility [44] of photochemical decomposition of lead bromide or lead chloride with the formation of atomic chlorine or bromine -- the active constituents of smog -- is suggested.

The presence of tetraethyl lead in gasoline has no appreciable effect on the content of carbon monoxide, oxides of nitrogen, and aldehydes in exhaust gases [45]. The data are somewhat contradictory as to the effect of TEL on the content of hydrocarbons in exhaust gases. For example, studies by the Ford Company showed that the addition of 0.78 ml/l of TEL leads to a 35 percent rise in the hydrocarbon content in exhaust gases [45]. In another paper [46], an increase of only 7 percent in hydrocarbon content was noted. Studies made on a single-cylinder engine [47] showed that TEL causes an increase in the hydrocarbon content in exhaust gases only in the combustion of paraffinic hydrocarbons. This increase does not occur in the presence of aromatic hydrocarbons (up to 40 percent).

The effect of the chemical composition of gasolines on the composition of exhaust gases has been studied very little and the available data are contradictory. Experiments with a single-cylinder engine showed [48] that in the combustion of isooctane and diisobutylene, the olefinic hydrocarbon content in exhaust gases is much higher than in the combustion of toluene. The maximum olefin content was found for $\alpha \approx 1$. Adding 25 percent n-heptane to toluene leads to an increase in the concentration of ethylbenzene of 1.9 times, a 1.9 times rise in the styrene content, and a 2.1 times rise in the dimethylacetylene content in exhaust gases.

It was of interest to compare the composition of exhaust gases when diisobutylene and isooctane were used. For $\alpha = 0.75$, the content of unburned diisobutylene in exhaust gases proved to be much less than the content of unburned isooctane in the same conditions. For $\alpha > 1$, the total content of olefin hydrocarbons in exhaust gases proved to be less than for operation using diisobutylene or for operation with isooctane. This result indicates the predominance in exhaust gases of secondary-origin hydrocarbons, whose presence is due to the temperature conditions of the combustion of the initial hydrocarbon.

Another study [49] showed that the CO content in exhaust gases does not depend on gasoline composition but is determined by mixture composition.

The amount of hydrocarbons in exhaust gases varied little in operation on gasolines of different compositions. But the content of unsaturated hydrocarbons in exhaust gases rose with the increased content of olefin hydrocarbons in the gasoline.

Unfortunately, no work has been done on the effect of the amount of aromatic hydrocarbons and their structure on the content of polycyclic aromatic hydrocarbons in exhaust gases. These studies are particularly vital owing to the growing content of aromatic hydrocarbons in commercial automotive gasolines.

The fractional composition of automotive gasolines evidently affects the toxicity of exhaust gases only little, but on the other hand, it significantly affects overall toxicity. The use of light gasolines with high saturated vapor pressure leads to a rise in the amount of hydrocarbons entering the atmosphere from fuel tanks, carburetors, etc. Tests showed that using gasoline with a saturated vapor pressure of 0.41 kg/cm^2 instead of 0.68 kg/cm^2 in the area of Los Angeles reduced atmospheric pollution by 59 percent [50].

Studies were made on several ways of lowering the toxicity of exhaust gases by replacing automotive gasoline with gaseous fuel (propane, ethane, etc.). It was found that replacing gasoline with propane significantly reduces the carbon monoxide content in exhaust gases. The use of propane made it possible to lower the hydrocarbon content in exhaust gases by more than 50 percent compared with the minimum hydrocarbon content occurring when gasoline was used. Here the content in exhaust gases of hydrocarbons active in photochemical synthesis leading to smog formation is significantly reduced.

The content (in percent by weight) of hydrocarbons [51] in exhaust gases (95 percent throttle open, $\alpha = 0.93$, CFR one-cylinder engine) is given below:

	For operation on propane	For operation on gasoline
Methane*	2.6	8.0
Ethane*	0.0	0.0
Ethylene	13.6	8.2
Acetylene*	4.7	6.1
Propane*	73.5	0.0
Propylene	4.7	5.7
Butane*	0.7	0.4
Butene-1	0.2	4.6

[Display continued on following page]

	For operation on propane	For operation on gasoline
Pentane*	0.1	14.8
Pentene-1	0.1	2.9
C_6 (saturated + aromatic hydrocarbons)	0.1	40.8
C_6 (olefinic hydrocarbons)	0.1	8.5
Total	100.0	100.0
Content of hydrocarbons participating in photochemical reactions	18.8	70.7

---

* Hydrocarbons not participating in photochemical reactions.

It has been established that the toxicity of exhaust gases depend on the amount of deposits accumulated in the combustion chambers of the gasoline engine. With increasing carbon deposits over the 60 hours of testing, the content of nitrogen oxide in exhaust gases rose from 0.28 to 0.44 percent. The content of hydrocarbons in exhaust gases climbed from 0.002 to 0.007 percent in 142 hours of engine operation. After these deposits were removed from the engine, the content of nitrogen oxide and hydrocarbons in exhaust gases dropped to their initial values [52].

It must be noted that if the knock resistance of a gasoline does not meet the engine requirements and in some regimes the engine operates with knocking, the toxicity of its exhaust gases can be severely changed. In particular, the content of oxides of nitrogen [28] in gases, when knocking appears in the engine, rises by 1.5-2 times (Fig. 142). True, here the content of carbon monoxide and hydrocarbons is somewhat reduced [43], but overall the appearance of knocking leads to higher toxicity of exhaust gases.

The rapid growth in the number of vehicles operating in the cities of industrially advanced countries made it necessary to formulate measures to lower the toxicity of exhaust gases. One American scientist wrote: "One of two things: either people do what has to be done for the air to have less smog, or smog will change things so that there will be fewer people on earth."

At the present time, several methods are used in battling exhaust gas toxocity: engine tuning, organization of the combustion process, installing different kinds of final ignition devices and traps, modifying fuel composition, and using additives. All these methods have, unfortunately, disadvantages and do not lead to the total elimination of exhaust gas toxicity. Accordingly, in many countries the maximum allowable exhaust gas toxicity levels have been restricted by legislation.

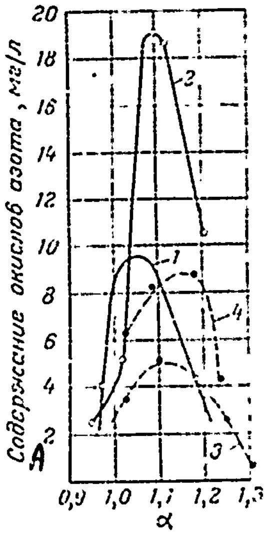


Fig. 142. Dependence of nitrogen oxide content in exhaust gases [29] on the mixture composition for normal and knock combustion in an engine. Compression ratio 8.5; charge factor 0.9;crank speed 1200 rpm:

1 — Ignition advance 20° before TDC without knocking
2 — Ignition advance 20° before TDC with knocking
3 — Ignition advance 15° before TDC without knocking
4 — Ignition advance 14° before TDC with knocking

Key: A — Content of nitrogen oxides, mg/l

One way of reducing the content of carbon monoxide and the oxides of nitrogen in exhaust gases, besides design measures intended to organize the combustion process, is recommended : tuning carburetor engines to operate on lean mixtures (10-13 percent leaner than the stoichiometric composition). Thus, the concentrations of CO and NO in exhaust gases will become the same and the possibility of the following reaction taking place will appear:

$$2NO + 2CO \rightleftarrows N_2 + 2CO_2$$

as the result of which no toxic constituents of exhaust gases will remain. True, this reaction in ordinary conditions proceeds very slowly, therefore studies are underway to select appropriate catalysts [53].

One of the effective methods of lowering the concentration of the oxides of nitrogen in exhaust gases in carburetor engines is water injection into the intake system. Tests showed that this method can lower the concentration of the oxides of nitrogen by 90 percent [54, 55].

The use of final ignition devices and absorbers encounters difficulties owing to their being poisoned by lead compounds when ethyl gasolines are used.

In recent years, the tendency to replace ethyl gasolines with gasolines not containing antiknocks has appeared in other countries. The question of increasing the cost of high-octane gasolines when they are produced without the use of lead antiknocks is being examined. In this respect the manganese antiknock can prove useful, which extends the completeness of combustion, lowers exhaust gas toxicity, and does not cause poisoning of the catalysts in the final ignition devices.

In the past decade, norms for the maximum allowable content of toxic compounds in exhaust gases were developed and confirmed by legislation in several countries of Europe, in the United States, and Japan. Special methods and programs of testing motor vehicles for exhaust gas toxicity were developed. The so-called travel cycles were adopted, including operating an engine in idle, accelerating the vehicle, deceleration, and traveling at constant speed. These cycles were developed on the basis of a detailed study of the travel of a motor vehicle in urban conditions. The total duration of the "California" travel cycle is 15 minutes, and 13 minutes for the European cycle. Mean data on exhaust gas toxicity over several travel cycles are used in the calculations.

In 1966 norms were set in California on the toxic components of exhaust gases: the content of carbon monoxide must not exceed 1.5 percent by weight, and that of hydrocarbons -- not more than $275 \cdot 10^{-4}$ percent by weight, regardless of the engine capacity. However, later the requirements placed on engines of different size were differentiated: for 0.82-1.64 liter engines the carbon monoxide content must be not more than 2.3 percent by weight, and not more than $410 \cdot 10^{-4}$ percent by weight for hydrocarbon content; the values for 1.64-2.29 liter engines are 2.0 and 350, and for engines with capacity greater than 2.29 liters — 1.5 and 275, respectively. It is anticipated that in the near future these norms will be even stricter — — 1.5 and $180 \cdot 10^{-4}$ percent by weight, respectively. It has been proposed to introduce a norm also on the content of the oxides of nitrogen (not more than $350 \cdot 10^{-4}$ percent by weight). All researchers agree that there must be absolutely no carcinogenic products in exhaust gases. However, this problem has not yet been dealt with by legislation [56-59]. In the USSR, the use of ethyl gasolines in ten of the largest cities was forbidden by legislation for the first time in the world (for example, Moscow, Leningrad, Kiev), and in two climatic zones (the Black Sea littoral of the Caucasus and the Crimea).

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[To Chapter Ten]

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CHAPTER ELEVEN

COMMERCIAL GASOLINES

Modern commercial automotive gasolines as a rule are prepared by blending several components. Producing them directly at processing facilities is fraught with economic difficulties and therefore is virtually not used at the present time. Blending (compounding) components makes it possible to produce a commercial product with the required quality, by rationally employing the properties of each component. Compounding permits, for example, in making commercial gasolines, employing gasoline fractions with inadequate knock resistance, which is then improved by adding high-octane components. Additionally, preparing commercial gasolines by compounding makes it possible to most fully utilize all the resources of gasoline fractions available at the refinery.

The main indicators determining the component composition of commercial gasolines include the requirements on knock resistance and fractional composition. Sometimes the content of particular components in commercial gasolines is limited by the requirements placed on sulfur content, chemical stability, etc. Additives improving one or several operating properties are added to all modern commercial automotive gasolines.

Gasolines of the USSR

The quality of domestic commercial automotive gasolines is standardized. With the advances made in motor vehicle engine building and a stiffening of requirements on the quality of gasolines used, changes and supplements have been introduced into the standard and from time to time responsible agencies re-examine the standard as a whole. For example, in 1956 the standard for automotive gasolines (GOST 2084-56) providing for the production of four grades of gasoline A-66, A-72, A-74, and A-76 took effect. Subsequently, owing to the building of engines with higher compression ratios (the vehicle ZIL-111 and Chayka), a gasoline with a higher octane number was required. Based on these requirements, Ekstra gasoline was developed, which is produced according to special specifications. In 1967, a new standard (GOST 2084-67) took effect, governing automotive gasolines of the grades A-66, A-72, A-76, AI-93, and AI-98 in production (Table 101).

This diversity of grades of commercial gasolines is related to the diversity of specifications imposed on the knock resistance of fuels for the engines of vehicles in use. A-66 gasoline is intended for the operation of engines in vehicles already removed from production or else being produced in limited numbers (ZIL-150, ZIL-164, GAZ-51, etc.). In Moscow, all these vehicles are being successfully operated on A-72 gasoline and there is no A-66 gasoline in the service station pumps of the capital. However, in the country as a whole the proportion of vehicles of the older models in the motor vehicle park is quite high and the demand for A-66 gasoline in 1970 was about half of the total requirement of automotive gasolines.*

A-72 and A-76 gasolines are intended for use in engines of vehicles which are currently produced by the automotive industry on a mass scale. A-76 gasoline must in the near future become the most common gasoline for engines of trucks, since it is used in ZIL-130 and GAZ-66 vehicles, whose production is steadily rising.

AI-93 gasoline is intended for use in the engine models for passenger cars (Zhiguli, Moskvich-412, and Volga GAZ-24), and also for existing (Ural-375) and prospective truck engines. AI-98 gasoline must meet the specifications of prospective engines for higher-class passenger cars.

In addition to gasolines for domestic consumption, refineries produce automotive gasolines for export (Table 102).

The specifications on exported automotive gasolines contain requirements only on the main indicators. All the remaining indicators and the special requirements are negotiated with the importer in a special delivery contract.

The number and quality of components used in producing given grades of commercial automotive gasolines differs widely and, in particular, depends on the refinery processing capabilities. The components composition of commercial gasolines of the same grade and kind, but from different refineries, can also vary, all the more so in that the chemical composition of commercial gasolines is not regulated by a standard. Even gasolines of the same grade produced by the same refinery at different times can differ in components composition owing to preventive maintenance of individual facilities, modification of refinery program in producing products, etc.

General correlations in the production of commercial gasolines of various grades are reflected in Table 103.

A-66 gasolines are prepared by compounding generally two components —— straight-run and thermal cracking gasolines. Components prepared by catalytic processes are added in small amounts at some refineries. Low-

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* B. S. Federov, Khimiya i Tekhnologiya Topliv i Masel, No 1 (1971).

Table 101. Requirements on the quality of automotive gasolines for internal consumption

Показатель 1	А-66	А-72	А-76	АИ-93	АИ-98
Детонационная стойкость, пункты, не менее 2					
ОЧИМ 3	Не нормируется 16			93	98
ОЧММ 4	66	72	76	85	89
Содержание ТЭС 8/кг, не более 5	0,60	0,00	0,41	0,82	0,82
Фракционный состав, °C * 6					
$t_{н.к.}$, не ниже 7	17 ниже 35	35	35	35	35
t_{10}, не выше 8	79 (65) *	70 (55)	70 (55)	70 (55)	70
t_{50}, » »	125 (115)	115 (100)	115 (100)	115 (100)	115
t_{90}, » »	195 (160)	180 (160)	180 (160)	180 (160)	180
$t_{к.к.}$, не выше ** 9	205 (185)	195 (185)	195 (185)	195 (185)	195
Содержание фактических смол, мг/100 мл, не более 10					
на месте производства при поставке 11	7	5	5	5	5
» » потребления 12	15	10	10	7	7
Индукционный период окисления (на месте производства, до этилирования), мин, не менее 13	450	600	900	900	900
Содержание серы, %, не более 14	18 0,15	19 0,12	20 0,10	21 0,10	22 0,10
Цвет 15	Оранжевый	Отсутствует	Зеленый	Синий	Желтый

Remark. The saturated vapor pressure of all grades of gasoline must not exceed 500 mm Hg for summer gasoline, and 700 mm Hg for winter gasolines; the acidity must not be more than 3 mg KOH/100 ml. All fuels must withstand the copper strip test and must not contain water-soluble acids and alkalis, mechanical impurities, or water.

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* The indicator for winter gasoline is given in parentheses.

** The mass of the residue in the flask after evaporation must not exceed 1.5 percent for all gasolines, while the total mass of the residue and the loss resulting from evaporation must not be more than 4.0 percent (of the total amount of produce).

Key:
1 -- Indicator
2 -- Knock resistance, points not less than
3 -- ONRM
4 -- ONMM
5 -- TEL content g/kg [text has 8/kg, obviously an error], not more than
6 -- Fractional composition
7 -- $t_{i.b}$, not less than
8 -- not more than
9 -- $t_{e.b}$, not more than**
10 -- Content of existent gums, mg/100 ml, not more than
11 -- at the site or production upon delivery
12 -- at the site of consumption
13 -- Oxidation induction period (at the site of production, before ethyl fluid addition), minutes, not less than.
14 -- Sulfur content, percent, not more than
15 -- Color
16 -- Not standardized
17 -- below 35
18 -- Orange
19 -- Absent
20 -- Green
21 -- Dark blue
22 -- Yellow

Table 102. Requirements on the quality of automotive gasolines intended for export

Показатель 1	А-83	А-87	А-90	АИ-93 2	А-95	АИ-98 3	А-100
Детонационная стойкость, пункты, не менее 4							
ОЧИМ 5	83	87	90	93	95	98	100
ОЧММ 6	78	83	84	85	86	89	90
Содержание ТЭС, мл/кг, не более 7	0,60	0,70	0,73	0,73	0,73	0,75	0,75
Фракционный состав, °С 8							
$t_{н.к}$, не ниже 9	—	—	38	40	46	40	40
t_{10}, не выше 10	75	75	70	70	70	70	70
t_{50}, » »	120	120	110	120	110	110	110
t_{90}, » »	180	180	180	180	160	160	160
$t_{к.к}$, » » 11	190	190	190	190	180	180	180
Масса остатка после испарения, % 12	1,5	1,5	1,5	1,5	1,5	1,5	1,5
Остаток + потери, % 13	2,5	2,5	3,0	3,0	3,0	3,0	3,0
Цвет 14	15 Оранжевый	16 Оранжевый или розовый	17 Бледно-розовый	18 Оранжевый	18 Оранжевый	19 Розовый	19 Розовый

Remark. The saturated vehicle pressure of all grades of gasolines must not be more than 450 Hg, acidity must not be more than 1 mg KOH/100 ml, existent gum content must not be more than 2 mg/100 ml, the oxidation induction period must not be longer than 500 minutes, sulfur content not more than 0.05 percent; all gasolines must pass the Doctor test and the copper strip test and must not contain water-soluble acids and alkalis, mechanical impurities, or water.

Key: 1 -- Indicator
2 -- AI-93 gasoline
3 -- AI-98 gasoline
4 -- Knock resistance, points, not less than
5 -- ONRM
6 -- ONMM
7 -- TEL content, ml/kg, not more than
8 -- Fractional composition
9 -- $t_{i.b}$, not less than
10 -- not more than
11 -- $t_{e.b}$, not more than
12 -- Mass of residue after evaporation
13 -- Residue + losses
14 -- Color
15 -- Orange
16 -- Orange or pink
17 -- Pale-pink
18 -- Orange
19 -- Pink

Table 103. Most typical variants of component composition (in weight percent) of domestic commercial automotive gasolines

Компоненты 1	А-66			А-72			А-76			АИ-93 2			АИ-98**** 3
	1*	2*	3*	1**	2**	3**	1***	2***	3***	1****	2****	3****	
Бензин прямой перегонки 4	55	51	55	30	10	5	20	7,5	—	23	18	—	—
Бензин термического крекинга 5	45	34	29	—	10	5	10	8,0	15	—	—	—	—
Бензин каталитического крекинга 6	—	13	6	70	—	70	—	7,0	30	—	30	—	—
Бензин платформинга 7													
обычного режима 8	—	—	8	—	75	15	70	60,0	40	—	—	—	—
жесткого » 9	—	—	—	—	—	—	—	—	10	77	47	65	65
Газовый бензин 10	—	—	2	—	3	5	—	7,5	3	—	2	—	—
Бутан-бутиленовая фракция 11	—	2	—	—	2	—	—	—	2	—	—	—	—
Алкилат (алкилбензин) 12	—	—	—	—	—	—	—	10,0	—	—	3	35	35

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* TEL content not more than 0.6 g/kg of fuel.
** Nonethyl gasoline.
*** TEL content not more than 0.41 g/kg of fuel.
**** TEL content not more than 0.82 g/kg of fuel.

Key: 1 — Components
2 — AI-93 gasoline
3 — AI-98 gasoline****
4 — Straight-run gasoline
5 — Thermal cracking gasoline
6 — Catalytic cracking gasoline
7 — Platforming gasoline
8 — of usual regime
9 — of drastic regime
10 — Natural gasoline
11 — Butane-butylene fraction
12 — Alkylate (alkyl gasoline)

boiling components of the natural gasoline type, spent butane-butylene fraction, etc., are resorted to in producing A-66 gasolines of winter grade.

A-72 gasolines are prepared by using a large amount of catalytic-process components. Generally, catalytic cracking and usual-regime platforming gasolines are utilized. Straight-run and thermal cracking gasolines are used in small amounts.

A-76 gasolines are essentially A-72 gasolines, only with ethyl fluid added. Therefore the component composition of A076 and A-72 gasolines is very similar. In the production of A-76 gasoline in nonethyl form, the content of catalytic-process components is somewhat increased, and at times drastic-regime platforming gasoline is used as is, or else after toluene has been extracted from it.

AI-93 gasolines are prepared only by blending components produced in catalytic processes. The base component of AI-93 gasoline is drastic-regime platforming gasoline. To meet the requirements on fractional composition, to this gasoline is added straight-run gasoline and low-boiling hydrocarbons and fractions. To boost the uniformity of octane number distribution by fractions, alkylate is added to drastic-regime platforming gasoline. It must be noted that in preparing AI-93 gasoline grades, especially in the nonethyl form, the question arises as to the very high content of the aromatic hydrocarbons in commercial gasoline (about 60 percent). Unfortunately, thus far no norm has been set on the content of aromatic hydrocarbons in commercial gasolines, however operating experience suggests that their content must not exceed 40-45 percent.

AI-98 gasolines in ethyl form can be produced by adding ethyl fluid to AI-93 nonethyl gasoline. In the nonethyl form, AI-98 gasoline can be prepared by blending 50 percent alkyl gasoline and 50 percent toluene.

To improve operating properties, additives are introduced to commercial automotive gasolines, and for higher octane numbers -- ethyl fluid: a blend of the antiknock -- tetraethyl lead -- with a scavenger. At the present time two kinds of ethyl fluids are added to domestic gasolines -- R-9 fluid with a bromide scavenger and A fluid, in which some of the bromide scavenger is replaced with a chloride scavenger (up to 6 percent or up to 14 percent chloride scavenger). All domestic ethyl fluids are colored yellow and an additional amount of the dye of the required color is added to the gasolines.

Thermal and catalytic-cracking gasoline distillates are stabilized with the addition of anti-oxidants. In practice, the lignoresin anti-oxidant (in amounts up 0.15 percent) FCh-16 anti-oxidant (0.05-0.10 percent), and p-oxydiphenylamine (0.01 percent) are used.

Since 1967 the domestic petroleum refining industry has not produced plain automotive gasoline; all gasolines are divided into winter and summer grades. Winter grade gasoline is intended for use in the northern climatic zone in all seasons, and in the central climatic zone -- from 1 October to 1 April. Summer grade gasoline is used in the southern climatic zone in all seasons, and in the central climatic zone -- from 1 April to 1 October. Thus, only one kind of gasoline is used in the northern and in the southern climatic zones the year round, and two kinds -- in the central climatic zone.

As a rule, all commercial automotive gasolines are released from oil refineries with a quality reserve for the main indicators. The smallest quality reserve usually is present for knock resistance. The octane number of commerical gasolines either corresponds exactly to the specified requirements, or else exceeds them by tenths of an octane point. It must be noted that during transportation, storage, and delivery of gasolines, as a rule their octane numbers change but little. However, in the practice of utilizing high-octane gasolines, there are often times when gasolines with octane number below the specified requirements reach users. The main reason for this situation is the blending of high-octane gasolines with low-octane gasolines in the delivery of gasolines to the user owing to inadequate cleaning of motor vehicle tanks, storage tanks, filling pump pipelines, etc. Considering the high requirements of modern motor vehicles on the knock resistance of the fuels used, the octane number of gasolines, especially high-octane, must be regularly monitored.

The TEL content in commercial gasolines is usually below the maximum norm set by the standard requirements.

In fractional composition, commercial automotive gasolines have a very substantial quality reserve, which makes it possible to use fresh gasolines to correct the quality of unfit gasolines for this indicator.

The sulfur content in commercial automotive gasolines can fluctuate from 0.01 percent to 0.3 percent, although the requirements in the standard (GOST 2084-67) provide for producing gasolines with a sulfur content not higher than 0.15 percent. The point is that over several years the State Committee on Standards of the USSR Council of Ministers has permitted* by special resolution to allow several refineries to produce gasolines with a 0.3 percent sulfur content.

As a rule, fresh gasolines have a significant quality reserve in existent gum content and acidity. However, both indicators can change with time, particularly the existent gum content, therefore they must be regularly monitored.

The prospects for expanding the direction of commercial automotive gasolines in our country are related to an increase in the proportion of high-octane gasolines produced at the expense of low-octane. To increase the knock resistance of commercial gasolines, new facilities for catalytic reforming, alkylation, isomerization, and other processes where high-octane components are produced are being introduced at oil refineries. High-octane gasolines as a rule have, in addition to octane number, higher quality also with respect to several other indicators: lower content of total and mercaptan sulfur, lower corrosiveness and gum content, higher chemical stability, etc. Thus, the operating qualities of gasolines in the future will improve in virtually all indicators. Expansion of the selection of additives for gasolines and an increase in their effectiveness must be expected in the near future, which will permit higher vehicle operating reliability and longevity.

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* A. A. Gureyev and D. M. Aronov, Standarty i kachestvo, No. 4 (1968).

The plant manual with which each motor vehicle is furnished indicates the grade of gasoline on which the engine successfully passed long-term plant tests and which is the main grade of fuel for this vehicle. In the absence of the principal grade, vehicles can be operated on other grades of automotive gasolines that have high antiknock properties. Experience shows that automotive gasolines operate successfully on A-72 gasoline instead of A-66, and on A-76 instead of A-72 gasoline. Here it must be remembered that no substantial improvement in engine performance occurs in these changes, but the cost of high-octane gasolines is higher than low-octane.

In several cases, when gasolines with high-octane number are used in engines with low compression ratio, valve scorching and other operating troubles were observed.

Use of gasolines with lower knock resistance than specified in the vehicle manual is unacceptable, since it leads to scorching of the cylinder blockhead gasket, increased wear, and sometimes even fracturing of parts.

In the absence of automotive gasolines, when necessary aviation gasolines or their blends can be used for some time (Table 104).

It must be noted that even B-70 aviation gasoline does not fully measure up to the requirements of automotive gasolines designed for A-66 gasoline. This gasoline [B-70] has a higher 10 percent distillation temperature, therefore, its starting properties are poorer than automotive gasolines. Other grades of aviation gasolines contain a high TEL content (three to four times greater than is permitted for automotive fuels).

A constant, narrowly determined ratios of fuels for preparing substitutes cannot be recommended in view of the significant fluctuations in the quality indicators of commercial samples. One must bear in mind that substitutes can be used only for a restricted period of time; lubricating oil is desirably replaced more often in this event, than specified by the instructions for the given vehicle.

Foreign gasolines

In socialist countries, as in the USSR, automotive gasolines are produced in accordance with the requirements of statewide standards (Table 105).

In the capitalist countries, automotive gasolines are produced by individual companies based on their specifications (Table 106). In addition to company conditions, there are also statewide standards for delivery of gasolines, for example, by military departments.

Table 104. Requirements on domestic aviation gasolines

Показатели 1	Б-100/130	Б-95/130	Б-91/115	Б-70
Детонационная стойкость, пункты, не менее 2				
ОЧММ 3	98,6	95	91	70
Содержание ТЭС, г/кг, не более 4	2,7	3,3	2,5	—
Фракционный состав, °С 5				
$t_{н.к.}$, не ниже 6	40	40	40	40
t_{10}, не выше 7	75	82	82	88
t_{50}, не выше 8	105	105	105	105
t_{90}, не выше 9	145	145	145	145
$t_{97,5}$, не выше 10	180	180	180	180
$P_н$, мм рт. ст. 11				
не менее 12	240	220	220	—
не более 13	360	360	360	360
Йодное число, г I_2/100 г бензина, не более 14	10	10	2	2
Содержание ароматических углеводородов, % 15	—	—	—	12—20
Содержание фактических смол, мг/100 мл бензина, не более 16	3	3	3	2
Цвет 17	19 Ярко-оранжевый	20 Желтый	21 Зеленый	22 Бесцветный
Содержание п-оксидифениламина, % 18	0,004 — 0,005	0,004 — 0,005	0,004 — 0,005	—

Remark. The acidity of aviation gasolines of all grades must not be more than 1 mg KOH/100 ml of product; the crystallization-onset temperature must not be higher than -60° C; the sulfur content must not be more than 0.05 percent by weight; all gasolines must pass the corrosion test (with a copper strip), must not contain water-soluble acids and alkalis, mechanical impurities, or water, and must also be clear.

Key: 1 — Indicators
2 — Knock resistance, points, not less than
3 — ONMM
4 — TEL content, g/kg, not more than
5 — Fractional composition
6 — $t_{i.b}$, not less than
7 — not higher than
8 — not higher than
9 — not higher than
10 — not higher than
11 — P_{sat}, mm Hg
12 — not less than
13 — not more than
14 — Iodine number, g I_2/100 g of gasoline, not more than
15 — Content of aromatic hydrocarbons
16 — Existent gum content, mg/100 ml of gasoline, not more than
17 — Color
18 — Content of p-hydroxydiphenylamine
19 — Bright orange
20 — Yellow
21 — Green
22 — Colorless

Table 105. Automotive gasolines of several socialist countries (requirements in standards)

1 Страна	2 Стандарт	3 Марка бензина	4 ОЧИМ	5 ОЧММ	6 Содержание ТЭС, г/кг, не более	7 Фракционный состав, °C				12 $P_{н}$, мм рт. ст.*	13 Содержание серы, вес. %, не более	14 Цвет
						8 t_{10}, не выше*	9 t_{50}, не выше	10 t_{90}, не выше	11 $t_{к.к.}$, не выше			
15 Болгария	21 ОТН–МХМ № НХ-2–67 22	А-78	78	73	0,45	70 (65)	115	180	195	450 (600)	0,05	Синий 23
		А-86	86	79	0,8	70 (65)	115	180	195	450 (600)	0,05	Красный 24
		А-96	96	91	2,5	82	105	145	180	220 (360)	0,05	—
16 Венгрия	MSZ 19950–68	E-76	76	72	0,8	70	125	180	200	500	0,10	Розовый 25
		E-86	86	78	0,8	70	120	180	205	500	0,05	Красный 24
		ESZ-92	92	85	0,8	65	115	180	205	600	0,05	Зеленый или синий 26
		ESZ-98	98	90	0,9	60	110	180	205	490	0,05	Зеленый
17 ГДР	TGL 6428	VK-84	84	80	0,6	70	—	180	—	530 (610)	0,03	Желтый
		VK-94	94	88	0,6	70 (15%)	100 (35%)	180	—	530 (610)	0,03	Красный 24
18 Польша	PN–66/K-96025	*Etilina* 78	78	76	1,2	75	135	185	200	530 (610)	0,15	Голубой 29
		Etilina 94	94	88	1,0	75	130	180	200	530 (610)	0,15	Желтый 28
19 Румыния	STAS-176–65	75/R (70/M)	75	70	—	79	145	195	205	500	0,05	—
		90/R (80/M)	90	80	—	70	120	180	205	500	0,05	—
20 Чехословакия	CSN 656505	BA-90	90	—	0,06 **	67	115	180 (95%)	210	600	0,05	Оранжевый 30
		BA-96	96	—	0,07 **	70	115	180 (95%)	210	600	0,10	Зеленый 27

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* For summer gasolines; the indicators for winter gasoline are given in parentheses.

** In percent by volume.

Key: 1 — Country
2 — Standard
3 — Grade of gasoline
4 — ONRM
5 — ONMM
6 — TEL content, g/kg, not more than
7 — Fractional composition
8 — Not higher than *
9 — Not higher than
10 — Not higher than
11 — $t_{e.b}$, not higher than
12 — P_{sat}, and Hg
13 — Sulfur content, percent by weight, not more than
14 — Color
15 — Bulgaria
16 — Hungary
17 — GDR
18 — Poland
19 — Romania
20 — Czechoslovakia
21 — OTN-MKhM
22 — No NKh-2-67
23 — Dark blue
24 — Red
25 — Pink
26 — Green or dark blue
27 — Green
28 — Yellow
29 — Blue
30 — Orange

Table 106. Automotive gasolines of the most advanced capitalist countries (actual indicators for 1970)

Сорт бензина 1	ОЧИМ 2	ОЧММ 3	Содержание ТЭС, г/кг 4	Давление насыщенных паров, мм рт. ст. 5	Содержание серы, вес. % 6	7 Фракционный состав, °С				
						8 $t_{н.к.}$	t_{10}	t_{50}	t_{90}	9 $t_{к.к.}$
США 10										
Супер 11	102,4	91,6	1,5	510	0,01	32	49	101	162	197
Премиальный 12	100,1	92,1	1,4	570	0,02	30	46	100	161	203
Обычный 13	94,2	86,3	1,3	565	0,04	31	46	94	162	209
Англия 14										
Пять звездочек 15	100,5	89,3	1,2	500	0,02	36	50	101	157	192
Четыре звездочки 16	99,5	88,7	1,0	540	0,03	33	50	103	159	196
Три звездочки 17	96,7	86,9	0,9	470	0,04	35	52	99	157	192
Две звездочки 18	92,8	85,3	1,0	460	0,03	33	52	98	157	192
Франция 19										
Премиальный 12	98,3	88,0	1,0	440	0,02	32	56	109	151	186
Обычный 13	90,5	85,0	1,0	440	0,02	33	51	86	150	156
ФРГ 20										
Премиальный 12	99,3	89,5	0,9	520	0,04	32	51	102	160	[illegible]
Обычный 13	92,5	85,5	0,8	540	0,05	31	53	95	160	[illegible]
Италия 21										
Премиальный 12	98,7	89,5	1,2	490	0,05	36	51	101	155	[illegible]
Обычный 13	88,0	83,0	1,4	490	0,05	35	50	86	158	[illegible]

Key:
1 — Grade of gasoline
2 — ONRM
3 — ONMM
4 — TEL content , g/kg
5 — Saturated vapor pressure, mm Hg
6 — Sulfur content, percent by weight
7 — Fractional composition
8 — $t_{i.b}$
9 — $t_{e.b}$
10 — United States
11 — Super
12 — Premium
13 — Regular
14 — Great Britain
15 — Five stars
16 — Four stars
17 — Three stars
18 — Two stars
19 — France
20 — Federal Republic of Germany
21 — Italy

In most countries, it is customary to subdivide gasolines by grades in relation to their octane numbers. In many capitalist countries two grades of automotive gasolines are produced -- premium and regular. In the United States, FRG, and several other countries a third grade of gasoline of increased quality is also produced -- "super gasoline." In a number of countries, the entire motor vehicle park is provided with the same grade of gasoline. In Great Britain, a new classification of gasolines was introduced -- by the number of stars, and four grades of fuel are used. The octane numbers of gasolines produced in the capitalist countries are quite high and are, according to the Research Method, 83-94 (regular), 95-100 (premium), and above 100 (super gasoline).

However, in recent years in several countries the question has been raised as to whether mass-produced gasoline could have lower octane numbers, but on the other hand contain no lead antiknock; this measure is designed to lower the toxicity of exhaust gases. In particular, in 1971 it was proposed in the United States to reduce the octane number of regular grade gasoline from 94.2 to 91.0. This provided for about 95 percent of 1971 model vehicles having a lower compression ratio than 1970 models (8.66 instead of 9.40) and their knock resistance requirements can be satisfied with regular gasoline, with an octane number of 91.0. It is planned that premium gasolines will remain ethyl, but their demand will be curtailed.

At the present time, in the capitalist countries most commercial automotive gasolines (97.5 percent) are produced in the ethyl form. Tetraethyl lead and tetramethyl lead are used in ethylation, and compounds of bromine or a mixture of compounds of bromine and chlorine are used as scavengers. As a rule, each grade of gasoline is colored differently. The dye is added to the ethyl fluids.

The content of lead antiknocks in gasolines currently produced in capitalist countries is significantly higher than in gasolines in the USSR. This circumstance must be borne in mind when operating domestic vehicles on foreign gasolines, since scorching of exhaust valves, increased deposits in combustion chambers, etc., are possible.

The sulfur content in foreign gasolines as a rule is hundredths of a percent. About 90 percent of all gasolines in capitalist countries contain less than 0.1 percent sulfur.

In fractional composition in saturated vapor pressure, foreign automotive gasolines have two fundamental distinctions from domestic. The first is that as a rule they contain more low-boiling fractions than gasolines of the USSR. Gasolines with a saturated vapor pressure of 600-700 mm Hg and a 10 percent distillation temperature not above 50° C are successfully used in numerous countries.

The second feature of the fractional composition of gasolines in capitalist countries is that they have increased end-boiling points. This is evidently associated with the extensive use of catalytic reforming gasolines, whose high-boiling fractions have good antiknock properties.

Noteworthy is the low saturated vapor pressure of gasolines used in high-altitude countries. Use of these gasolines prevents the formation of vapor locks in the fuel feed system.

In most countries, automotive gasolines are divided into winter and summer grades based on their fractional composition and the saturated vapor pressure. In addition, regional gasolines are produced in a number of countries. Thus, in the United States the entire country is divided into three climatic zones, based on ASTM specifications, in each of which gasolines with the optimal fractional composition are used.

The chemical stability of northern foreign gasolines, as a rule, is not standardized, but the use of effective synthetic anti-oxidants ensures high stability of commercial fuels. Besides antiknock and anti-oxidant additives, in several countries anticorrosion, anti-deposit, anti-icing, detergent, and other kinds of additives are used in gasolines.