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FUELS FOR JET ENGINES

By

Ya. B. Chertkov, G. F. Bol'shakov and
Ye. I. Gulin

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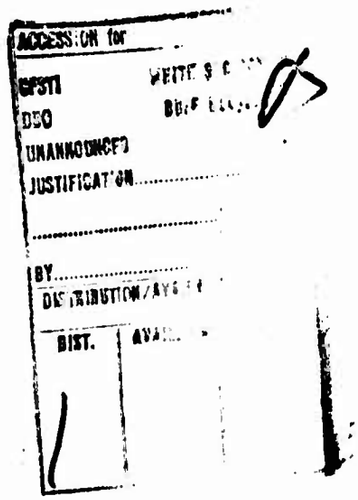

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BY: Ya. B. Chertkov, G. F. Bol'shakov and Ye. I. Gulin

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FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH

DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}
rot	curl
lg	log

The book contains information on the chemical composition and operational properties of jet fuels; data on the composition and properties of jet fuels, on the changes occurring in the process of prolonged storage of fuels, their transportation, and application on aircraft are generalized. Experience in the improvement of the operational properties of jet fuels by means of additives is given.

The book is intended for engineers and scientific personnel working in the field of the chemistry and application of jet fuels and can be used by students of special higher and secondary educational institutions.

INTRODUCTION

In the last fifteen years the technical equipment of aviation has been absolutely changed. Aircraft with piston engines are almost completely replaced by aircraft with air-breathing jet engines. The speed of flight of jet transport aircraft has approached the speed of sound and many aircraft fly at speeds considerably exceeding that of sound.

In addition to the passenger liners TU-104, IL-18, and AN-10, recently delighting the whole world with their flight specifications, such air ships as the TU-124, TU-114 and IL-62 have arrived on the scene. The transport role of jet aviation increases rapidly. The population of the country readily uses the services of the Civil Air Fleet, the air lines of which have girdled the country with a dense network. On long-range international lines Soviet aircraft and their crews have carried themselves well.

Rapid quantitative growth and qualitative improvement of jet aviation continues.

The consumption per hour of fuel in contemporary jet aircraft constitutes several tons and more. The fuel weight exceeds 50% of the gross weight of the aircraft. In spite of this, huge speeds and load capacities ensure that contemporary aircraft with air-breathing jet engines possess greater economy than was the case during operation of aircraft with piston engines.

Fuels for jet aviation are obtained from crude oil.

The development of jet aviation can be judged by the changes in recent years in the structure of consumption of petroleum products.

For instance, available data testify to the fact that in the United States the quantity of jet fuel expended for military purposes occupies first place, exceeding

by almost twice the expenditure of such fuels as black oil intended for the Navy (Table 1).

Table 1. Consumption in the United States of Petroleum Fuels for Military Purposes, Thousands of Tons*

Fuels	Actual expenditure				Assumed expenditure		
	1959	1960	1961	1962	1963	1964	1965
Jet fuel	14 600	14 230	15 300	15 200	16 100	16 700	16 800
Aviation gasoline. .	5 660	4 400	4 175	4 060	4 000	3 780	3 740
Automotive gasoline .	2 020	2 020	2 100	2 050	2 180	2 230	2 230
Diesel and other distillate fuels . . .	3 000	3 150	3 480	3 620	3 660	3 710	3 760
Naval fuel	8 920	8 070	8 420	8 780	8 750	8 750	8 630
All	34 200	31 870	33 475	33 730	34 690	35 170	35 160

*Inst. Petrol. rev., 15, No. 178, 316, 1961; World Petrol., 33, No. 1; 36, 1962; World Petrol. Statistics, 1960; Oil and Gas j., 59, No. 44, 99, 1961; Stromont D. Oil and Gas j., 59, No. 3, 56, 1961.

The nonmilitary consumption of jet fuel in the United States in 1962 constituted approximately 8 million tons and the consumption of jet fuel for military and civil needs exceeded 20 million t. An intense increase in the quantity of jet fuel consumed by civil aviation is anticipated.

In the development of jet aviation the Soviet Union has forged ahead of other countries, including even the United States. The performance and technical data of Soviet military and civil aircraft are higher than the corresponding characteristics of aircraft of the capitalistic countries.

Qualitative and quantitative growth of aviation is inseparably connected with an increase in the requirements for quality of fuels.

During the writing of this book we set as our goal to acquaint the reader with the properties of jet fuels and also with problems arising in connection with the increase in production and consumption of jet petroleum fuels and the increasing requirements of contemporary aviation as to their quality.

The authors express their great gratitude to Professor A. F. Dobryanskiy for his preliminary examination of the manuscript, useful critical remarks, and practical advice.

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CHAPTER I

SORT GRADING OF JET FUELS AND REQUIREMENTS FOR THEIR QUALITY

Jet fuels constitute chiefly products of straight run distillation of crude. With good low-temperature properties (low freezing point, low viscosity at low temperatures) jet aviation requires fuels with high heat of combustion and good burning qualities. Such requirements are met by a mixture of kerosene and ligroin fractions. The kerosene fraction is a component part of diesel fuels and its yield on crude is small. The necessity of increasing resources and reducing the cost of jet fuels has led to the application of certain grades of the wide fractional composition, representing a mixture of the gasoline, ligroin, and kerosene fractions of crude petroleum.

It is calculated that for production of jet fuel of wide fractional composition [illegible] of all processed petroleum in the United States can be used, but for the production of kerosene of a quality satisfactory for this purpose, only 6-8% of this oil is usable.

The effort to coordinate the cost and resources of fuel on the one hand and the requirements for fuel quality presented by the ever growing intensity of operation of engines on the other hand have led the majority of countries to have available several grades of jet fuels for different assignments.

The majority of jet engines can work on kerosene and on fuel of wide fractional composition. Fuels of wide fractional composition are at present the bulk utilized on a large part of aircraft with subsonic speeds. In conditions of great altitude, owing to the raised vapor pressure the losses of such fuel become considerable, which leads to a lowering of flying range and, consequently, of economy in the operation of aircraft. Owing to the distinction in densities, energy charges of

equal volumes of the fuels of wide fractional composition and fuels representing the ligroin-kerosene fraction are strongly distinguished. The fuel with the greater density is characterized by greater energy content per unit of volume. The latter is very important for aircraft with considerable flying range, starting their flight with a maximum fuel load in the tanks.

The operation on fuel of wide fractional composition of aircraft flying at a great height with speeds close to or exceeding the speed of sound apparently is impossible.

Such aircraft require fuels which meet specific requirements, including the smallest possible vapor pressure and high volume heat of combustion.

The need for fuels necessary for supersonic flights at present is small. In 1961 it was determined in the United States to be 1,830,000 tons a year [2]. With the development of such forms of transport the need for new fuels will increase.

The changes observed in the development of jet aviation permit us to assume the following classification of fuels for it (Table 2).

Table 2. Classification of Contemporary Fuels for Air-Breathing Jet Engines

Parent fractions for production of fuels	Aircraft with	
	top speed (M*)	height of flight, km
Gasoline-ligroin-kerosene fractions.....	Up to 1	Up to 15
Ligroin-kerosene fractions.....	Up to 1.5	Up to 20

*Mach number (M) is the relation of speed of flight of a vehicle to the speed of sound, equal to about 1194.5 km/hr at 0°C and [standard] atmospheric pressure [3].

Such a classification of fuels, composed in the most general form, will, clearly, be definitized in the future. Its advantage consists in the fact that it permits us, even at present, to determine with greater exactness the requirements for the quality of jet fuels, depending upon their assignment, and consequently to give technical and economic appraisals of the sources and methods of obtaining them and also of resources and cost.

Proceeding from peculiarities of exploitation of flight vehicles and conditions of the working process of air-breathing jet engines, to guarantee reliable and unfailing operation of engines on all regimes, the jet fuel should:

– be reliably pumped along the fuel supply system at high and low temperatures;

– be completely evaporated in the combustion chambers;

– ignite in wide limits of composition of the fuel mixture, with a small period of delay of ignition;

– burn stably, completely, at a high rate during a large surplus of air without the formation of scale;

– have high heat of combustion both by weight and by volume;

– not corrode components of the fuel system;

– have high stability in conditions of storage, transportation, and change;

– have sufficient antiwear properties (especially for fuels of facilitated fractional composition).

For jet fuels applied in supersonic vehicles, of special significance, along with those shown, are the following specific requirements: high thermooxidizing stability and minimum volatility during heating.

The quality of propellants is subjected to constant improvement. New constants appear for quality control; they reflect the increased requirements of aviation engineering. In place of the GOST's 4138-49 (for fuel T-1), 7149-54 (for fuel TS-1), and 8410-57 (for fuel T-2) the GOST 10227-62 has been affirmed; it contains increased requirements for certain old indices (acidity, content of mercaptan sulfur, existent gums, ash content) and along with this introduces new (although now optional) indices of quality (determination is obligatory, but the index itself is not standardized). For instance, new quality constants are introduced: thermal stability of fuel and content of elemental sulfur.

Some of the quality indices of fuels characterize their energy properties, inflammability, and burning in the engine. But the larger part of the indices are directed towards limitation of the negative influence of nonhydrocarbon impurities as a source of instability of fuel, not only in conditions of ordinary storage but also (which is very important) in conditions of operation of aircraft.

Table 3 gives the technical requirements for quality of jet fuels of the Soviet Union and the All-Union Government Standards [GOST's] for methods applied for characterizing the quality of fuels.

For comparison, we give the technical requirements for the quality of fuels for transport jet aviation of the United States (Table 4) in accordance with the standard ASTM-D 1655-61 T [4].

Table 3. Technical Requirements for Quality of Fuels of Straight Run Distillation for Aviation Jet Engines [GOST 10227-62, GOST 9145-59 (T-5)]

Indices	Norms by brands				Test Methods
	T-1	TS-1	T-2	T-5	
Density ρ_4^{20}, no less than...	0.800	0.775	0.775	0.845	GOST 3900-47
Heat of combustion, lowest, kcal/kg, no less than.....	10,250	10,250	10,300	10,250	GOST 5080-55
Fractional composition, °C:					
initial boiling point					
not over.....	150	150	–	–	
not under.....	–	–	60	195	
up to 200°C there evaporates (in %) not over...	–	–	–	2	
10% evaporated, max.....	175	165	145	225	
50% evaporated, max.....	225	195	195	–	GOST 2177-59
90% evaporated, max.....	270	230	250	–	
98% evaporated, max.....	280	250	280	315	
residue and loss, %, not over.....	2	2	2	2	
Viscosity, kinematic, cs:					
at +20°C,					
not over.....	–	–	–	5.0	
not under.....	1.50	1.25	1.05		
at -40°C,					
not over.....	16	8	6	60	GOST 33-53
Smoke point, mm, not less than.....	20	25	25	–	GOST 4338-48
Acidity, mg KOH/100 ml, not over.....	0.7	0.7	0.7	1.0	GOST 5985-59
Pressure of saturated vapors, mm Hg, not over.....	–	–	100		GOST 1756-52 or GOST 6668-53
Flash point in closed crucible, °C, not under.....	30	28	–	–	GOST 6356-52
Temperature of beginning of crystallization, °C, not over.....	-60	-60	-60	-60	GOST 5066-56 (without dehydration of fuel)
Iodine number, g iodine/100 g, not over.....	2	3.5	3.5	3	GOST 2070-55 or GOST 8997-59
Content of aromatic hydrocarbons, %, not over.....	20	22	22	22	GOST 6994-54
Thermal stability at 150°C for 4 hr, mg/100 ml.....	Not standardized, determination obligatory.				GOST 9144-59
Content of existent gums, mg/100 ml, not over.....	6	5	5	5	GOST 1567-56

(Table 3 Continued)

Indices	Norms by brands				Test Methods
	T-1	TS-1	T-2	T-5	
Total sulfur content, %, not over.....	0.1	0.25	0.25	0.1	GOST 1771-48
Content of mercaptan sulfur, %, not over.....	–	0.005	0.005	–	GOST 6975-57
Content of hydrogen sulfide	Absence				On indicator with lead acetate
Content of elemental sulfur	Not standardized, determination obligatory.				GOST 9494-60 or GOST 9558-60
Copper strip corrosion.....	Sustains without change in color of strip				GOST 6321-52
Content of water-soluble acids and alkalis.....	Absence				GOST 6307-60
Ash content, %, not over	0.003	0.003	0.003	0.005	GOST 1461-59
Content of mechanical impurities and water	Absence				

Table 4. Technical Requirements for Quality of Fuels for Jet Engines of Transport Aviation of the U. S. (ASTM-D 1655-61 T)*

Property	Norms by brands			ASTM test method
	"A"	"A-1"	"B"	
Density at 15.6°, g/ml,				
not under.....	0.7753	0.7753	0.7507	D-287
not over.....	0.8299	0.8299	0.8017	
Fractional composition, °C,				
10% evaporated, not over.	204.4	204.4	–	
20% evaporated, not over	–	–	143.3	
50% evaporated, not over	232.2	232.2	187.8	
90% evaporated, not over	–	–	243.3	
final boiling point, °C.	287.8	287.8	–	
residue and losses, %, not over.....	1.5	1.5	1.5	
Pressure of saturated vapors, mm Hg, not over.	–	–	155	D-323
Flash point in covered crucible, °C,				
not under.....	43.3	43.3	–	D-56
not over.....	65.6	65.6	–	
Temperature of beginning of crystallization [freezing point?], °C, not over...	-40	-58	-60	D-1477
Pour point, °C, not over..	-40	–	–	D-97
Kinematic viscosity at -34.44°C, cs, not over..	15	15	–	D-455

*This table is a retranslation of the Russian version, rather than a copy of the English original. The Russian format and the metric units are retained; terms are translated so as to agree with the remainder of this translation (e.g., "Density" for "Gravity," etc.) but are basically in the same form as in the original ASTM standard [Tr. Ed. note].

Table 4 (Continued)

Property	Norms by brands "A"	"A-1"	"B"	ASTM test method
Net heat of combustion, kcal/kg, not under.....	10223	10223	10223	D-1405 or D-240
Copper strip corrosion:				
3 hr at 50°C, not over..	No. 1	No. 1	–	D-130
2 hr at 100°C, not over	–	–	No. 1	
Total acidity, mg KOH/g, not over.....	0.1	0.1	–	D-130
Total sulfur, %, not over.	0.3	0.3	0.3	D-1266
Mercaptan sulfur, %, not over.....	0.003	0.003	0.003	D-1323 or D-1219
Water tolerance, vol. change, ml, not over....	±1	±1	±1	D-1094
Existent gums, mg/100 ml fuel, not over.....	7	7	7	D-381
Gum by oxidation method [total potential residue] (16 hr), mg/100 ml, not over.....	14	14	14	D-873
Thermal stability for 5 hr at preheater temp of 148.9°C and filter temp of 204.4°C, fuel flow rate of 2.72 kg/hr:				
filter pressure drop, mm Hg, not over.....	300	300	300	D-1660
preheater deposit, in scale div., not over	3	3	3	
Aromatics, vol. %, not over.....	20	20	20	D-1319
Olefins, vol. %, not over	–	–	5	D-1319
Combustion properties:				
luminometer number, not over.....	45	45	50	D-1740
or smoke point, mm, not under.....	25	25	–	D-1322
or smoke point, mm, not under.....	20	20	–	D-1322
and burning test, 16 hr	+	+	–	D-187
or smoke point, mm, not under.....	20	20	–	D-1322
and naphthalenes, %, not over.....	3	3	–	D-1840
or smoke volatility index (SVI*), not under.....	–	–	54	D-1322 or D-86

Introduction of various additives is permitted;

Additives used: antioxidants, corrosion inhibitors, metal deactivators; quantities and types must be declared by supplier and agreed to by the consumer.

*Smoke volatility index (SVI) – smoke point (mm) +0.42 of volume of fuel (%) boiling at temperature under 204.4°C.

Three grades of fuel are distinguished:

type "A" – kerosene with high flash point;

type "A-1" – also kerosene, but with improved low-temperature characteristic;

type "B" – fuel of wide fractional composition.

In the USA technical norms for jet fuels, attention is drawn by the following. Along with greater amounts of acidity, existent gums, and sulfur than is allowed in the fuels of the Soviet Union, in the compulsory series for all commerical fuels their water tolerance, the tendency of fuels to oxidation, thermal stability (by the method of circulation at quite rigid conditions (150-200°)) and burning properties are controlled. It has been decided to use the various methods enumerated in the specifications for the appraisal of burning properties of fuels or their combinations. It is common to use these methods to control scale-forming ability of fuel and, as the index on which it in considerable measure depends, the content of bicyclic aromatic hydrocarbons (napthalenes).

There is a very simple method (D-1094) of evaluating water tolerance of a fuel, consisting in observation of the change of volume of distilled water after it is shaken up with fuel in a volume ratio of 1:4. This method is of interest also because after settling of the mixture one can judge by the color of the meniscus the content in the fuel of microcontaminations, which concentrate with such treatment on the boundary of the phases.

In the whole sum of the above-enumerated methods of control the boundaries of the quality requirements are determined, depending not only on the raw material and the method of production but also on the operational conditions in which the fuel is applied, including the zone of combustion.

In the United States jet fuels provision is made for the introduction of additives of various functions. The concentration of additives is small. Thus, an antioxidant it is permitted to use one of three additives: 2,6-ditertiary butyl-4-methylphenol ("iomol," "topanol-0"); 2,4-dimethyl-6-tertiary butylphenol ("topanol A"); and N, N'-di-sec-butyl-p-phenylenediamine, in quantities to 0.003-0.004 wt. %. The application of anticorrosive additives and deactivators of metal, for instance N,N'-disalicylidene-1,2-propanediamine, in quantities of less than 0.001 wt. % is permitted. Metal deactivators are added to fuels from which excess quantity of mercaptans has been extracted by treatment with copper salts (cuprous chloride), under whose influence mercaptans are turned into disulfides. With such treatment ions of copper can remain in the fuel, acting as catalysts to stimulate the oxidation of unstable

components of the fuel. By binding ions of copper in the form of complexes, metal deactivators prevent their negative influence.

Finally, additives can be added to jet fuels to prevent the formation of crystals of ice during fast cooling of the fuel. This phenomenon is very dangerous, inasmuch as ice in the form of small crystals can block the fuel filter, limiting or halting normal entry of fuel into the zone of combustion. As such an additive 0.1-0.3 vol. % ethyl cellosolve with 10% glycerine (Mil-I-27686) is added to fuel [5, 6]. Ethyl cellosolve (monoethyl ether of ethylene glycol) dissolves crystals of ice and with the moisture of the fuel gives an evenly distributed low-freezing mixture, passing with the fuel through the filter.

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C H A P T E R II

PHYSICAL PROPERTIES OF JET FUELS

Reliable work of aviation jet engines in many respects depends on physical properties of fuels. A great influence on the operational characteristics of engines is rendered by such physical properties of fuels as viscosity, fractional composition, saturated vapor pressure, density, and surface tension.

Temperature of fuel during application in contemporary aircraft can oscillate from -60 to +250°C. At supersonic speeds of flight fuel is heated; subsonic speed it is cooled. Fuel often fulfills auxiliary functions; for instance, it is used for cooling of certain units of the engines. In these conditions heat capacity, thermal conductivity, and heat of evaporation of fuels obtain great significance.

Physical properties of fuels are considered by designers during the creation of new aircraft.

Below information is given about certain physical properties of jet fuels.

Density

Density [gravity] of propellants has essential operational value: on it depends the endurance and flying range of aircraft. If we take as the basis a fuel with a density of 0.833, then the reduction in technical distance and technical endurance of flight with a decrease in the density of fuels can be calculated according to the following formulas:

$$\Delta L_{r.s} = \frac{V(1-1.2\varrho)}{\varrho}; \quad \Delta T_{r.s} = \frac{V(1-1.2\varrho)}{Q},$$

[r.p = h.f = horizontal flight]

where $\Delta L_{h.f}$ is change of horizontal range, km;

$\Delta T_{h.f}$ is change of duration of horizontal flight, hr;

V is total capacity of fuel tanks, liters;

ρ is density of fuel, g/cm^3;

q is fuel consumption, liters/km;

Q is consumption per hour of fuel on given conditions, liters/hr.

Density of jet fuels depends on their fractional and chemical compositions. With weighting of fractional composition and increase in the content of aromatic hydrocarbons the density of fuels increases.

Density of commercial jet fuels at ordinary conditions (+20°C) is bounded by the limits 0.77-0.85 g/cm^3 (Table 5).

Table 5. Density of Jet Fuels at Various Temperatures

Temperature, °C	Fuels			
	TS-1	T-1	T-2	T-5
—60	0,8347	0,8801	0,8267	0,9041
—50	0,8276	0,8734	0,8194	0,8973
—40	0,8206	0,8648	0,8119	0,8902
—30	0,8135	0,8561	0,8054	0,8834
—20	0,8066	0,8487	0,7969	0,8765
—10	0,7982	0,8400	0,7894	0,8694
0	0,7913	0,8345	0,7818	0,8623
+10	0,7841	0,8264	0,7753	0,8553
+20	0,7762	0,8197	0,7668	0,8483
+30	0,7686	0,8139	0,7593	0,8412
+40	0,7616	0,8088	0,7517	0,8344
+50	0,7531	0,8000	0,7432	0,8271
+60	0,7464	0,7942	0,7368	0,8203
+70	0,7371	0,7889	0,7297	0,8134
+80	0,7306	0,7819	0,7228	0,8075
+90	0,7241	0,7733	0,7156	0,8006
+100	0,7178	0,7671	0,7088	0,7931
+110	0,7103	0,7589	0,7019	0,7861
+120	0,7038	0,7513	0,6948	0,7797
+130	0,6968	0,7441	0,7010	0,7734
+140	0,6898	0,7388	0,7090	0,7655
+150	0,6800	0,7293	0,6738	0,7591
+160	0,6731	0,7202	0,6666	0,7513
+170	0,6665	0,7121	0,6598	0,7440
+180	0,6594	0,7034	0,6527	0,7364
+190	0,6516	0,6941	0,6454	0,7297
+200	0,6448	0,6813	0,6388	0,7221
+210	—	0,6776	—	0,7142
+220	—	0,6675	—	0,7061
+230	—	0,6584	—	0,6982
+240	—	0,6474	—	0,6905
+250	—	0,6373	—	0,6831
+260	—	0,6272	—	0,6742
+270	—	0,6171	—	0,6671
+280	—	—	—	0,6591

Note: For determinations of density we took specific fuels from crudes of certain deposits [8].

Table 5 gives experimentally determined values of density at temperatures from -60°C to the beginning of boiling. Density at higher temperatures was determined by means of calculations by the formula

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

where ρ_4^t is density at $t^\circ C$, g/cm^3;

ρ_4^{20} is density at $+20^\circ C$, g/cm^3.

The average temperature correction (γ) can be drawn from the preceding determinations and also determined by the formula [52]

$$\gamma = (18{,}310 - 13{,}233\,\rho_4^{20})\,10^{-4}.$$

As can be seen from Table 5, a change in the temperature of fuel by $50^\circ C$ leads to a change in the volume of fuel by 3-5%. There is practical interest in the further study of such a question as the servicing of aircraft with deeply cooled fuel directly before their start. This ensures a greater range of operation of the aircraft. In these cases there is no need to fear an increase in the volume of fuel with heating, inasmuch as its expenditure will exceed the increase in volume of fuel during heating.

Data [2] on the density of saturated vapor of fuel T-1 at different temperatures are given in Table 6.

Table 6. Density of Saturated Vapors of Fuel T-1 at Various Pressures and Temperatures

Temperature, °C	Pressure of saturated vapor, mm Hg	Density of vapor, $g/cm^3 \cdot 10^{-3}$	Temperature, °C	Pressure of saturated vapor, mm Hg	Density of vapor, $g/cm^3 \cdot 10^{-3}$
85,5	82,7	0,435	148,0	517,0	2,546
102,5	136,3	0,716	150,8	551,5	2,695
107,5	159,6	0,834	151,0	557,0	2,729
128,8	297,6	1,506	152,8	581,0	2,837
129,0	300,6	1,525	154,7	611,0	2,967
131,3	320,0	1,612	160,5	708,0	3,425
139,3	404,0	2,018	163,5	756,0	3,645
142,5	440,6	2,195	164,5	784,0	3,776
146,5	494,0	2,427	—	—	—

As can be seen from the given data, with an increase in the temperature and the pressure of saturated vapor the density of the latter increases. At a temperature of $+160^\circ C$ and pressure of 760 mm Hg the density of saturated vapor is almost 200 times less than the density of fuel T-1 in the liquid phase.

The density of jet fuels depends also on pressure: it increases with an increase in pressure (Fig. 1). However, the influence of pressure is small. Thus, at an increase in pressure of up to 100 atm density increases on the average by 2-3%. From Fig. 1 it is evident that with an increase in temperature the influence of pressure appears more strongly.

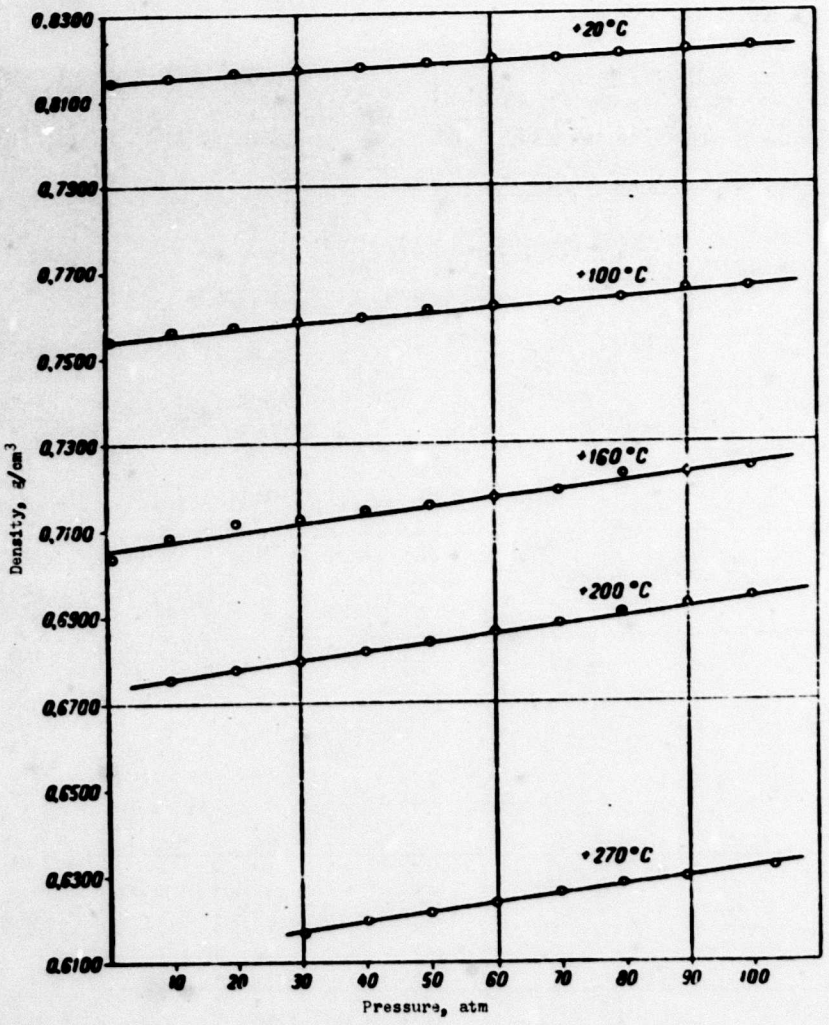

Fig. 1. Influence of pressure on density of fuel T-1 at various temperatures.

Fractional Composition

Jet fuels differ considerably in terms of fractional composition. The fractional composition of commercial jet fuels is given in Table 7.

Fuel T-2 evaporates within the limits 70-250°C. Owing to the introduction of gasoline fractions, the temperature of beginning of distillation of this fuel is considerably lower as compared to the others. This causes increased losses of fuel due to evaporation during high-altitude flights unless the fuel in tank is under pressure.

Fuel T-1 evaporates within the limits 140-280°C. The final boiling point of fuel TS-1 is somewhat lower than that of fuel T-1 and is within the limits 230-240°C. Limitation of the final boiling point of fuel TS-1 is caused by the fact that weighting the fractional composition of distillates worsens their low-temperature properties and increases the content of aromatic hydrocarbons, including bicyclic, as a

consequence of which hygroscopicity is raised; the content of sulfurous compounds is increased, resulting in worsening of thermooxidizing stability of fuels.

Table 7. Fractional Composition of Commercial Jet Fuels

Fractional composition	Fuels							
	T-1		TS-1		T-2		T-5	
	Temperature of vapor phase, °C	Temperature of liquid phase, °C	Temperature of vapor phase, °C	Temperature of liquid phase, °C	Temperature of vapor phase, °C	Temperature of liquid phase, °C	Temperature of vapor phase, °C	Temperature of liquid phase, °C
Beginning of boiling . .	144	170	140	171	70	126	195	215
10% Evaporates at . .	164	183	151	167	127	157	—	—
50% » » . .	202	220	174	188	172	192	247	260
90% » » . .	250	285	212	231	211	229	280	296
98% » » . .	280	307	230	250	248	284	292	323

Therefore expansion of fractional composition of fuel TS-1 by means of a fraction evaporating within the limits 250-280°C would considerably worsen the operational properties of the fuel.

Fuel T-5 has a relatively heavy fractional composition and evaporates within the limits 195-290°C.

Jet fuels are complicated mixtures of various hydrocarbons and heteroorganic compounds, as a consequence of which temperature of vapors does not coincide with the temperature of the liquid phase of the fuel in the process of evaporation (Table 7).

As can be seen from the given data, the temperature of the liquid phase during distillation is higher than the corresponding temperature of the vapor phase by, on the average, 20-25°C.

Frequently, for various technical calculations it is necessary to know the average boiling point of fuels. This temperature can either be determined by means of integration of the curve of fractional distillation or by calculating by the formula [52]

$$t_{cp} = \frac{1}{9}(t_1 + t_2 + \ldots + t_9),$$

[cp = av = average]

where t_1; t_2; ...; t_9 are average temperatures (°C) corresponding to boiling out of 10, 20, ..., 90% of the initial volume of fuel, °C.

Boiling point of fuel depends on pressure. This dependence is described by the following equation [52]:

$$\frac{T_{av}^{p}}{T_{av}} = Ap^{n},$$

where T_{av}^{p} is the average boiling point at pressure p, °K; T_{av} is the average boiling point at a pressure of 1 atm, °K; p is pressure, mm Hg (atm (abs.)); A and n are coefficients.

The values of the empirical coefficients A and n are given below:

Pressure p	A	n
20-100 mm Hg	0.63	0.063
100-760 mm Hg	0.58	0.082
1-5 atm (abs)	1.0	0.10

The formula permits determining the average molecular boiling point of fuels with an accuracy of 1%.

Pressure of Saturated Vapors

For jet fuels, which are complicated multicomponent liquids, the pressure of saturated vapors depends on the temperature, the ratio of the liquid and vapor phases, and concentration.

Fig. 2 gives data on the pressure of saturated vapors of commercial jet fuels [2, 3]. The determination of the pressure of saturated vapors was conducted after removal from the fuels of water and gases. With weighting of fuels the pressure of saturated vapors decreases.

The ratio of the volumes occupied by the liquid and vapor phases has an essential influence on the pressure of saturated vapors (Fig. 3). With an increase in the ratio of liquid and vapor phases the pressure of saturated vapors increases. As the true value one should take the pressure of saturated vapors at a ratio V_{liq}/V_{vap} when V_{vap} occupies an infinitely large volume.

For mathematical expression of the dependence of the pressure of saturated vapors of fuel on temperature, the Clausius-Clapeyron equation is often used [2, 3, 65]:

$$\lg p = B - \frac{A}{T},$$

where p is the pressure of saturated vapor, mm Hg (atm (abs)); T is absolute temperature, °K; A and B are constants determined experimentally.

Table 8 gives experimentally determined values of the coefficients A and B in the Clausius-Clapeyron equation [3].

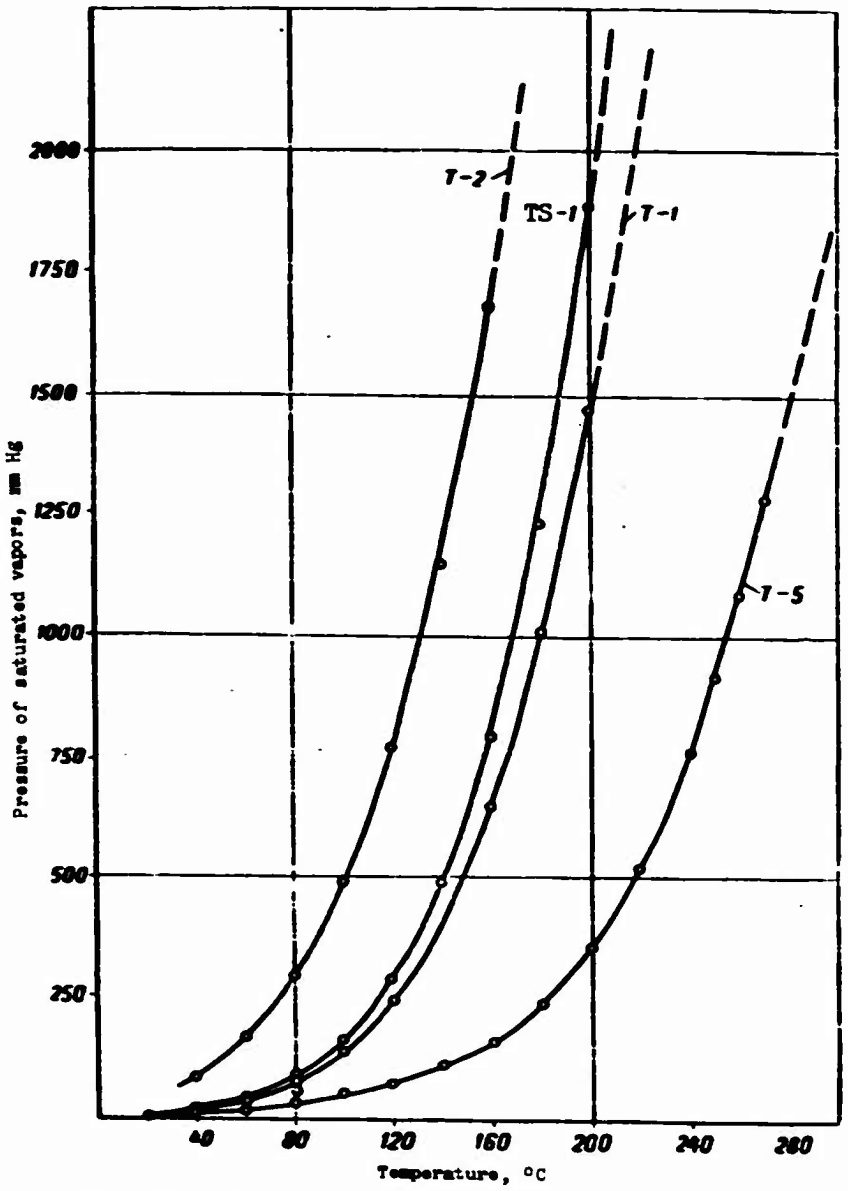

Fig. 2. Pressure of saturated vapors of commercial jet fuels at a ratio of liquid and vapor phases of 1:4.

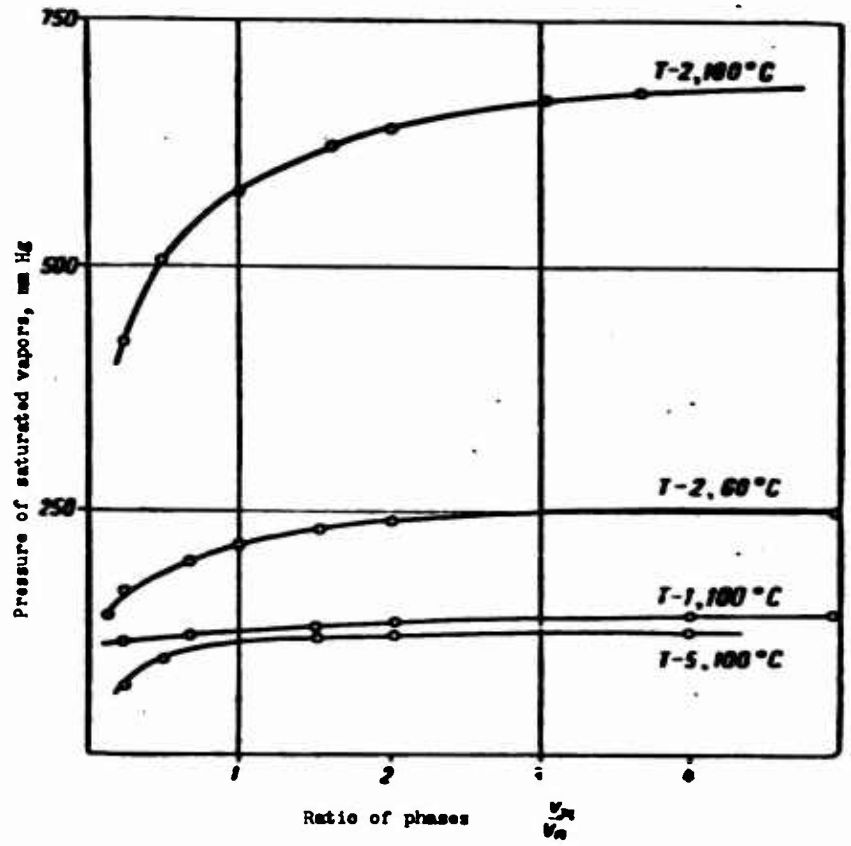

Fig. 3. Pressure of saturated vapors of fuels at various ratios of the liquid and vapor phases.
[ж = liq = liquid, п = vap = vapor].

Table 8. Values of Coefficients A and B for Calculation of the Pressure of Saturated Vapors by the Clausius-Clapeyron Equation

Jet fuels	Parent fuels			Degasified fuels		
	Temperature range °C	A	B	Temperature range °C	A	B
T-2	20—90 90—155	1090 1300	5,728 6,312	38—160	1436	6,522
TS-1	20—90 90—200	1080 1727	5,194 6,977	38—200	1954	7,411
T-1	20—90 90—20	816 1737	4,248 6,850	38—200	1853	7,089
T-5	20—100 100—200	638 1698	3,463 6,324	40—200	1886	6,694

Vapor pressure of fuels is lowered after the removal from them of gases. The graphic dependence $\lg p = f\left(\frac{1}{T}\right)$ deviates considerably from a straight line. This explains the introduction of two values of coefficients in the Clausius-Clapeyron formula (Table 8) during calculation of the vapor pressure of saturated vapors of one fuel in two temperature ranges.

The pressure of saturated vapors of fuels at 760 mm Hg and 0°C can be calculated by the formula [52]

$$\lg p = 11{,}3 - \frac{4770}{368 - t_s},$$

where t_s is the average boiling point of the fuel, °C.

Cloud Point and Freezing Point

The cloud point is that temperature at which the fuel starts to become cloudy. The turbidity of fuel during cooling is connected with the separation, in the first place, of microdrops of water and microcrystals of ice. This is explained by the fact that with a decrease in temperature the solubility of water in hydrocarbons decreases sharply and it precipitates from fuel in the form of the second phase.

The content of water in a fuel depends on external conditions (temperature, atmospheric humidity, and others); therefore the cloud point of fuels is different under different conditions and the fuel at the time of application has a different cloud point than it does in a period of storage. Obviously, we can agree with the opinion that the determination of the cloud point of jet fuels does not have practical value, although the operational significance of this index is great [5].

Table 9 gives [7, 8] data on the cloud points of commercial jet fuels and of hydrocarbon separated from them. As can be seen, the cloud points of aromatic hydrocarbons are considerably higher than those of the parent fuels. This is explained by the great hygroscopicity of aromatic hydrocarbons. The cloud points of alkane-cyclane hydrocarbons remain, for practical purposes, insignificant, inasmuch as they have low hygroscopicity.

Table 9. Freezing Point of Jet Fuels and Separated Hydrocarbon Groups

Fuel	Group chemical composition wt %				Temperature of beginning of crystallization, °C	Freezing point, °C	Cloud point, °C
	Aromatic hydrocarbons	Alkane hydrocarbons	Cyclone hydrocarbons	Unsaturated hydrocarbons			
Parent fuel	19,5	33,5	45,0	2,0	—64	—66	—53
Alkane-cyclane fraction ..	0	41,0	59,0	0	—62	—62	Not noted
Aromatic fraction	97,8	0,9	1,2	0,1	—76	—89	—17
TS-1							
Parent fuel	18,7	59,3	19,8	2,2	—62	—63	—41
Alkane-cyclane fraction' .	0	78,0	22,0	0	—55	—55	Not noted
Aromatic fraction	98,1	1,0	0,3	0,6	—84	—85 (fracture)	—12
T-2							
Parent fuel	19,6	57,1	21,6	1,7	—65	—68	Not noted
Alkane-cyclane fraction .	0	72,0	28,0	0	—60	—60	the same
Aromatic fraction . . .	95,3	1,8	0,8	2,1	—78	—91 (fracture)	—28
T-5							
Parent fuel	20,6	21,7	57,0	0,7	—61	—64	—55
Alkane-cyclane fraction .	0	48,6	51,4	0	—57	—57	Not noted
Aromatic fraction	98,0	0	1,0	1,0	—61	—67	—25

Under the temperature of the beginning of crystallization we understand the maximum temperature at which crystals are detected in the fuel by the naked eye.

For individual substances the temperature of beginning of crystallization coincides with their freezing point. Inasmuch as jet fuels are mixtures of hydrocarbons with different freezing points, crystal formation occurs in them in certain intervals of temperatures. First of all during cooling of jet fuels crystals of compounds with high freezing points are separated. These substances can be certain

hydrocarbons, heteroorganic compounds, and water. With an increase in molecular weight of hydrocarbons of fuels and, consequently, weighting of their fractional composition, the freezing point is increased. The structure of hydrocarbons has great significance. For hydrocarbons with identical molecular weights but different structures, the freezing point can be very different.

Among the hydrocarbons of jet fuels, alkane hydrocarbons of normal structure have high freezing points. The content of alkane hydrocarbons of normal structure in fuels is small, but even with small amounts of them the freezing point of fuels is increased. Thus after the addition of as little as 2% cetane to an isoparaffin fraction with limits of boiling 235-265°C, the freezing point of this fraction is increased from -75°C to -23°C [5]. With an increase in the branching of alkane hydrocarbons their freezing points drop. The lowest freezing points fall to alkane hydrocarbons of T- and П-shaped structure [6].

As compared to alkanes, cyclane hydrocarbons (especially with short asymmetrically arranged chains) have lower freezing points. The lowest freezing points in the hydrocarbons of jet fuels characterize monocyclic aromatic hydrocarbons with short branded lateral chains. With an increase in the length and a decrease of branching of lateral radicals of cyclane and aromatic hydrocarbons the freezing points of the latter increase.

Table 9 gives data [7, 8] on the freezing points of commercial jet fuels and of hydrocarbon groups separated from them.

From the data in Table 9 one can see that the temperature of the beginning of crystallization is several degrees higher than the freezing point. This difference increases with an increase in the content of aromatic hydrocarbons (Fig. 4) and attains a maximum for pure aromatic hydrocarbons. The temperature of beginning of crystallization and the freezing point of alkane-cyclane fractions of hydrocarbons coincide (Table 9). In absolute value the aromatic hydrocarbons have the lowest freezing points and the alkane-cyclane fractions of hydrocarbons have the highest. It is interesting to note that the aromatic hydrocarbons are characterized in actuality not by the freezing point, but by "fracture," as if of an amorphous substance at sufficiently low temperatures.

The assumption is advanced that the distinction in the temperature of beginning of crystallization and the freezing point depends not only on the hydrocarbon composition of fuels [5, 9, 10, 12, 13] but also on the presence of sulfurous compounds [14].

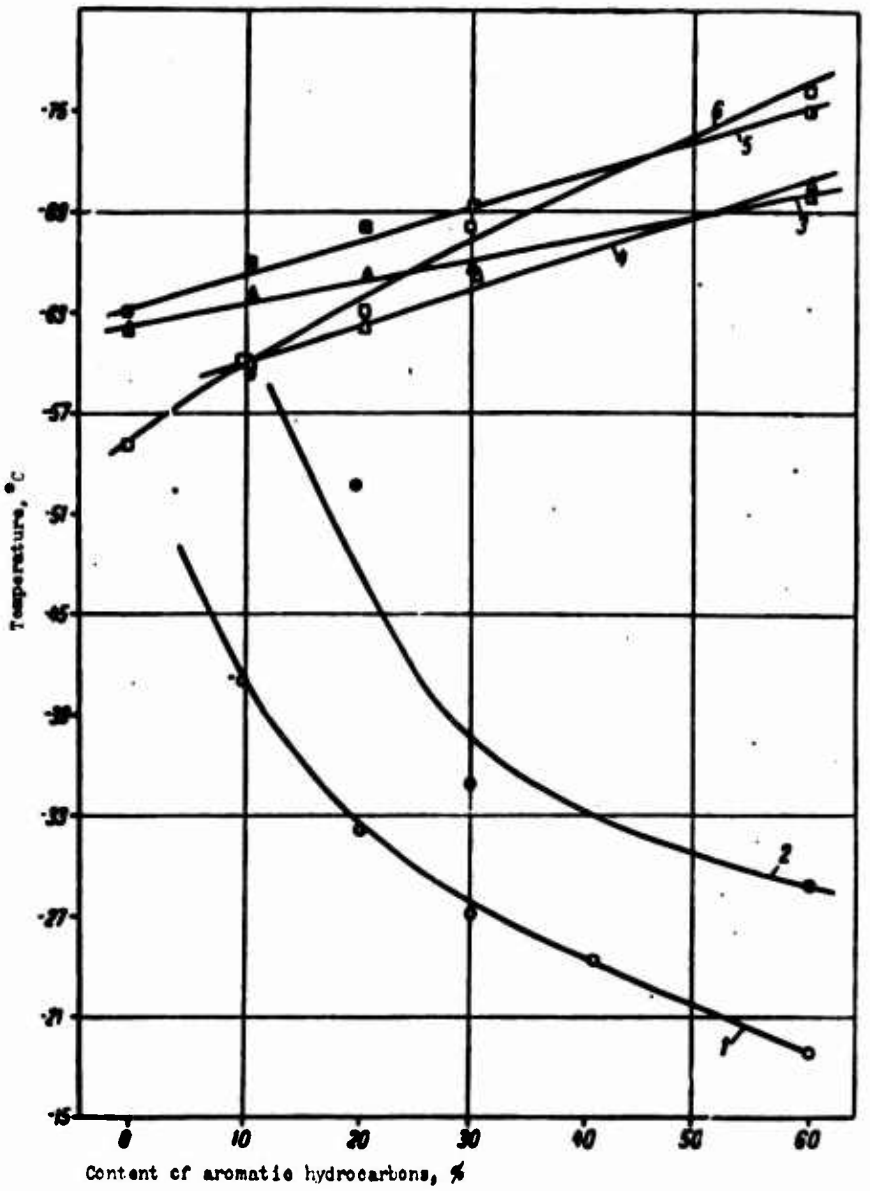

Fig. 4. Effect of aromatic hydrocarbons on cloud point, beginning of crystallization, and freezing point of the fuels T-1 and TS-1. 1 — cloudiness of fuel TS-1; 2 — cloudiness of fuel T-1; 3 — beginning of crystallization of fuel T-1; 4 — beginning of crystallization of fuel TS-1; 5 — freezing of fuel T-1; 6 — freezing of fuel TS-1.

The temperature of the beginning of crystallization of dry propellants is determined by the presence of alkane hydrocarbons of normal structure. The shape of the emanated crystals strongly depends on the chemical composition of the hydrocarbon medium [9, 10]. The rate of growth of crystals depends on several factors and is approximately expressed by the following formula [11]:

$$W = \frac{K}{\eta}(C - B),$$

where W is the rate of growth of a crystal;

K is a constant, depending on the rate of cooling and the character of agitation;

η is the absolute viscosity of the medium;

C is the concentration of paraffin, wt. %;

B is the solubility of paraffin at a given temperature, wt. %.

From this formula it follows that the rate of growth of crystals is directly proportional to the concentration of paraffin and is inversely proportional to the viscosity of the medium.

There is no single opinion about the mechanism of freezing of jet fuels at present. However, the majority of researchers consider that freezing of light petroleum products is caused by the loss from them first of all of alkane hydrocarbons of normal structure, which form groups of oriented molecules. These groups subsequently are centers of formation of nuclei of crystals [15].

The mechanism of the freezing of petroleum products at present is explained by two theories – crystallizational [16, 17, 18] and colloidal [19, 20, 21].

Obviously, it follows to recognize as most correct the opinion that freezing (crystallization) of petroleum products, depending upon external conditions and chemical composition, occurs either as a result of the formation of a crystal lattice or as a result of the formation of solvate shells (collodial structure) or supermicellar structure, or during the action of these three (or two) factors simultaneously [5].

The low-temperature properties of fuels depend on the chemical composition of the hydrocarbons. All classes of hydrocarbons which enter into the composition of jet fuels and which are evaporated at up to 200°C are crystallized at a temperature considerably below minus 60°C.

Monocyclic aromatic and cyclane hydrocarbons present in the composition of jet fuels and evaporating within the limits 200-300°C also congeal at a temperature considerably below minus 60°C. If they are cooled to minus 90-100° they gradually change mobility, congealing to a solid amorphous state; after this fracture of the thickened mass sets in, in connection with supercooling.

Of the hydrocarbons detected in jet fuels, alkane hydrocarbons of normal structure and bicyclic aromatic hydrocarbons with the number of carbon atoms in the lateral chains no more than 1-2, boiling at a temperature higher than 200°C, are crystallized at a temperature above minus 60°C.

Viscosity

With an increase in the molecular weights and boiling points of hydrocarbons their viscosity increases. Therefore fuels of type T-2 are characterized by lower viscosity than fuels of type TS-1, T-1 and T-5. Viscosity of jet fuels depends

also on temperature and the chemical composition of the fuel.

The influence of temperature on viscosity of standard fuels [28] is shown in Figs. 5 and 6. With a decrease in temperature the distinction in the viscosity of the fuels increases. Fuel T-5 becomes especially highly viscous: at a temperature of -60°C its viscosity attains 280-300 cs.

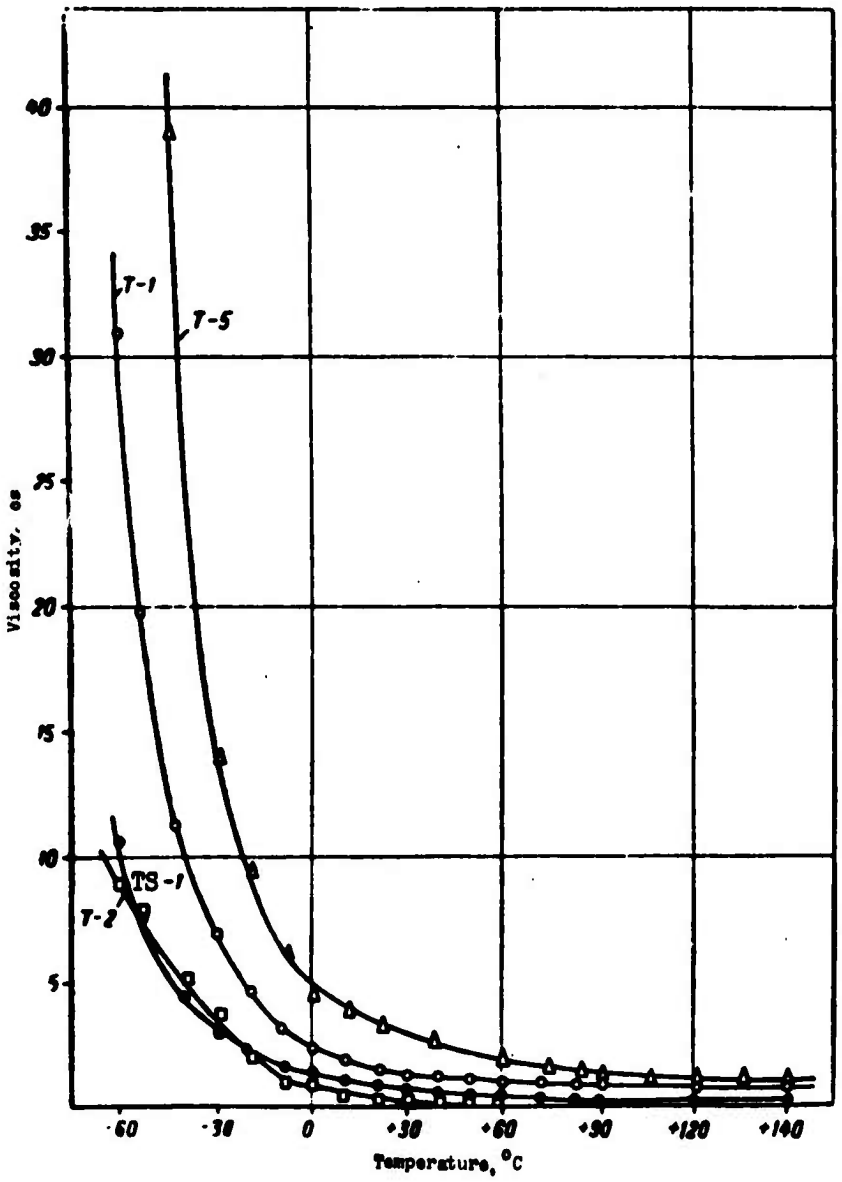

Fig. 5. Dependence of viscosity of jet fuels on temperature.

The effect of group chemical composition on the viscosity-temperature properties of jet fuels [7] is shown in Fig. 7. Alkane-cyclane fractions at positive temperatures have somewhat higher viscosity than aromatics. With a lowering of temperature this distinction decreases and with further cooling the viscosity of aromatic hydrocarbons sharply increases. With an increase in the content of aromatic hydrocarbons in the fuel the curve of the change of viscosity with temperature becomes steeper.

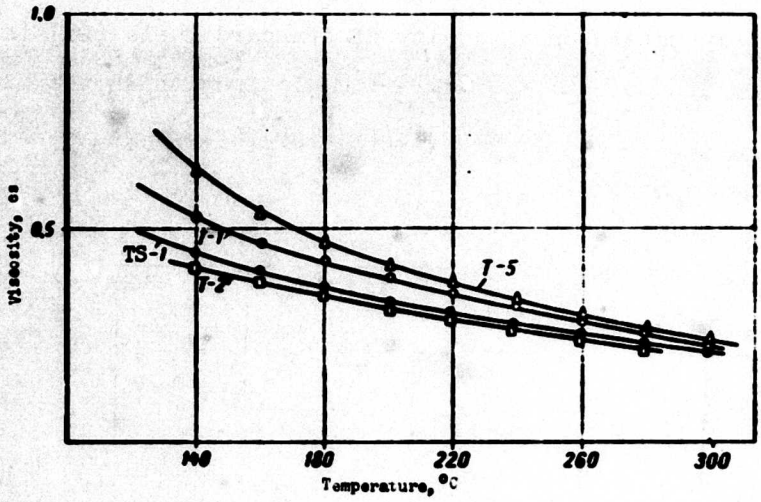

Fig. 6. Dependence of viscosity of jet fuels on temperature.

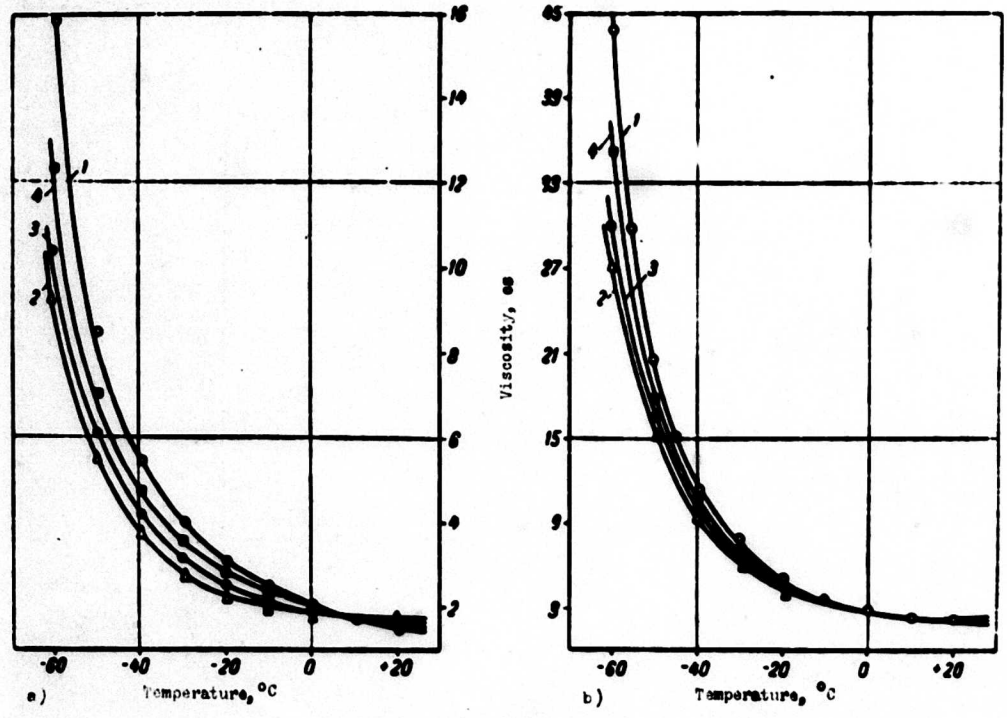

Fig. 7. Influence of group chemical composition on viscosity properties of jet fuels TS-1 (a) and T-1 (b). 1 — aromatic fraction; 2 — alkane-cyclane fraction; 3 — parent fuel with addition of 20% aromatic fraction; 4 —parent fuel with addition of 60% aromatic fraction.

With an increase in molecular weight the distinction in viscosity of hydrocarbon groups increases.

A study was made of the change of viscosity with temperature of hydrocarbons of 50-degree fractions, monotypic in chemical structure, separated chromatographically

from medium-distillate fuels (150-300°C) obtained from products of the refining of crudes of different deposits and, in one case, from products of hydrogenation of carbon.

Table 10 shows the dependence of viscosity properties of hydrocarbon fractions on the length of lateral chains and molecular weight with identical contents of rings in the molecule.

With an increase in the number of rings in a molecule of hydrocarbons with identical quantities of carbon atoms in the lateral chains, viscosity-temperature properties worsen (Table 11).

Table 10. Change of Viscosity Properties of Hydrocarbons, Depending upon Length of Aliphatic Chains of "Average" Molecule of Fractions

Origin of hydrocarbon fractions	Molecular weight	Number of rings in average molecule	Number of C-atoms of aliphatic chain	Walter coefficient n	Kinematic viscosity at temperature, cs				
					20° C	0° C	−20° C	−40° C	−60° C
Cyclane hydrocarbons									
Azerbaidzhan crudes									
I	219	1,20	8,0	4,22	8,09	17,53	54,12	273,4	899,70
II	183	1,19	6,0	4,30	4,43	8,65	21,30	85,23	707,85
III	168	1,20	4,8	4,05	3,00	5,03	10,61	29,85	135,60
IV	224	1,00	10,0	4,18	4,71	8,53	21,13	88,01	701,22
V	196	1,00	8,0	3,68	3,73	6,57	15,00	42,69	318,06
VI	167	1,03	5,6	4,00	2,91	4,95	10,44	30,38	154,46
VII	165	0,98	5,7	4,00	2,35	3,69	6,94	16,32	76,59
VIII	147	1,02	4,2	3,59	1,86	2,79	4,77	9,66	24,62
Aromatic hydrocarbons									
Azerbaidzhan crudes									
I	202	1,90	4,4	5,80	25,64	142,12	—	—	—
II	164	1,90	1,8	5,29	4,26	8,03	33,96	222,8	—
III	159	1,87	1,8	5,03	4,73	9,58	32,77	431,13	—
IV	154	1,92	1,2	5,03	4,94	11,09	38,12	—	—
V	172	1,17	7,1	4,49	2,65	4,26	9,82	32,73	196,20
VI	172	1,18	5,5	4,49	3,23	5,29	12,41	45,37	276,19
VII	164	1,19	4,8	4,49	2,81	4,74	10,50	34,77	277,14
VIII	151	1,16	4,2	4,50	2,02	3,11	7,00	19,50	78,29
IX	162	1,08	5,5	4,30	1,49	2,20	4,01	8,32	27,54
Privolzhskiye [Cisvolga] crudes:									
I	180	1,07	8,5	4,86	4,06	7,30	18,96	71,33	—
II	166	1,07	5,6	4,50	3,42	6,20	15,02	54,05	—
III	159	1,08	5,0	4,80	2,74	4,65	11,69	42,50	362,50
Privolzhskiye [Cisvolga] crudes	154	1,09	4,6	4,49	2,26	3,56	7,48	19,92	116,01
Far Eastern crudes .	130	1,05	3,3	4,22	1,49	2,19	3,71	7,71	24,89
Coal I	139	0,99	5,0	3,75	1,45	2,07	3,44	6,74	16,09

Table 11. Change of Viscosity Properties of Hydrocarbons, Depending upon the Quantity of Rings in "Average" Molecules of Fractions

Origin of hydrocarbons fractions	Molecular weight	Number of rings in average molecule	Number of C atoms in aliphatic chain	Walter coefficient m	Kinematic viscosity (at temperature) cs				
					20° C	0° C	—20° C	—40° C	—60° C
Alkane-cyclane fraction of hydrocarbons									
Groznyy crudes	111	0,59	4,1	3,27	0,86	1,09	1,44	2,13	3,43
Azerbaidzhan crudes:									
I	133	0,82	3,8	3,47	1,31	1,74	2,66	4,45	8,87
II	147	1,02	4,2	3,59	1,86	2,79	4,77	9,66	24,62
Coal I	170	1,32	4,2	4,00	2,76	4,35	8,55	23,79	—
Cisvolga crudes:									
I	121	0,29	6,5	3,39	0,97	1,22	1,74	2,69	4,63
II	132	0,38	6,7	3,68	1,24	1,67	2,59	4,39	9,40
Azerbaidzhan crude	159	0,79	6,3	3,59	1,87	2,70	4,58	9,93	31,0
Groznyy crude oil	164	0,83	6,4	4,00	1,93	2,96	5,16	10,97	—
Azerbaidzhan crudes ...	164	0,90	6,3	4,00	2,11	3,49	6,73	13,37	46,10
Aromatic hydrocarbons									
Cisvolga crude	128	0,94	4,2	3,75	1,09	1,46	1,99	4,30	7,49
Azerbaidzhan crudes:									
I.....	146	1,02	4,5	3,75	1,25	1,71	2,53	4,89	11,18
II	154	1,13	4,6	4,49	2,26	3,56	7,48	19,92	116,01
III	151	1,16	4,2	4,50	2,02	3,11	7,00	19,50	78,20
Far Eastern crude	157	1,20	4,4	4,49	2,87	4,64	9,68	29,75	235,06

For all hydrocarbon fractions the dependence of the kinematic viscosity on temperature is described with sufficient accuracy for practical purposes by the equation of Walter (see below). This permitted using the Walter coefficient m for a comparative appraisal of viscosity-temperature properties of hydrocarbon fractions. As is known, the magnitude of the coefficient m depends on the chemical composition of the mixture and characterizes its viscosity-temperature properties in a similar manner as the index of viscosity [75].

The basic components of jet fuels which satisfy, in terms of viscosity-temperature properties, contemporary requirements are monocyclic napthenic hydrocarbons with an average number of C-atoms in the lateral chain of no more than 4.2 and also monocyclic aromatic and alkane hydrocarbons of isomeric structure which do not congeal and freeze above a temperature of minus 60°C.

The content in the fuel of fractions of alkane hydrocarbons of normal structure, crystallizing at a temperature above minus 60°C, is limited only by the solubility of their crystals in the fuel.

The presence of monocyclic napthenic hydrocarbons with the number of C-atoms in the lateral chain of an "average" molecule of over 4.2 and of bicyclic napthenic and aromatic hydrocarbons is permissible in the case when the viscosity of the mixture of basic components of the fuel at minus 40°C is lower than the GOST permissible limit.

The most effective components, lowering the viscosity of fuel simultaneously at minus 20 and minus 40°C, are alkane hydrocarbons of normal and branched structure, not freezing down to a temperature of minus 60°C.

A decrease in the cyclic hydrocarbon content of the fuel lowers its viscosity at low temperatures. In this respect the removal of napthenic hydrocarbons is more effective than [removal] of the corresponding aromatics.

Viscosity at a temperature of +20°C can be determined by means of calculation by the equation [52]

$$\eta = at_{cp} + bt_{cp}^2 + ct_{cp}^3,$$

where η is dynamic viscosity, kg·sec/m^2; t_{av} is average boiling point, °C; a, b, c are coefficients, which for jet fuels constitute, respectively, $0.138 \cdot 10^{-4}$; $0.116 \cdot 10^{-6}$; $0.0398 \cdot 10^{-8}$.

This equation ensures obtaining results with an error of no more than 10%.

Several empirical equations for expressing the dependence of the viscosity of petroleum products on temperature have been proposed. The formula of Walter [23] is well known:

$$\lg\lg(\nu + 0{,}8) = p + m\lg T,$$

where ν is kinematic viscosity, cs; T is temperature, °K; p, m are constants.

There have been proposals to replace 0.8 by the coefficient 0.6 [24]. K. S. Ramayya [22] proposed the following equation:

$$\ln\eta = \left(C + \frac{D}{T}\right)^2,$$

where η is dynamic viscosity, poise; C, D are constants; T is temperature, °K.

There is the Bachinskiy formula, the validity of which was checked by Kopylov and Sirotina [2]:

$$\eta = \frac{A}{(t+\alpha)^n},$$

where η is dynamic viscosity, cp; t is temperature, °K; A, α, n are constants.

The values of the coefficients A, α, and n are given in Table 12.

Table 12. Value of Constants in the Bachinskiy Equation

Fuel	from −50 to +10°C			from +20 to +300°C		
	A	α	n	A	α	n
T-1	18.2	70	1,58	238.8	90	2,07
T-5	44.0	115	1,84	3319	76	2,53

Viscosity calculated by the equation $\eta = \frac{A}{(t + \alpha)^n}$ agrees well with experimental data.

The viscosity of jet fuels depends on pressure [41-44], and this dependence can be expressed by the equation [59]

$$\eta = \eta_0 (1 + \alpha p),$$

where η is dynamic viscosity in cp at a pressure of 1.033 kg/cm^2;

p is excess pressure, kg/cm^2;

α is a coefficient equal to ~0.001.

Viscosity increases noticeably only at pressures over 200-300 atm. The viscosity of naphthenic and aromatic hydrocarbons is changed the most with an increase in pressure, and that of alkanes least of all. For the calculations it is necessary to know the viscosity not only of the liquid fuels but also that of their vapors. Figure 8 presents data on the viscosity of the vapors of fuels T-1 and T-5 [2]. The viscosity of the vapors of the fuels was investigated in a capillary viscosimeter with a circulation loop [25].

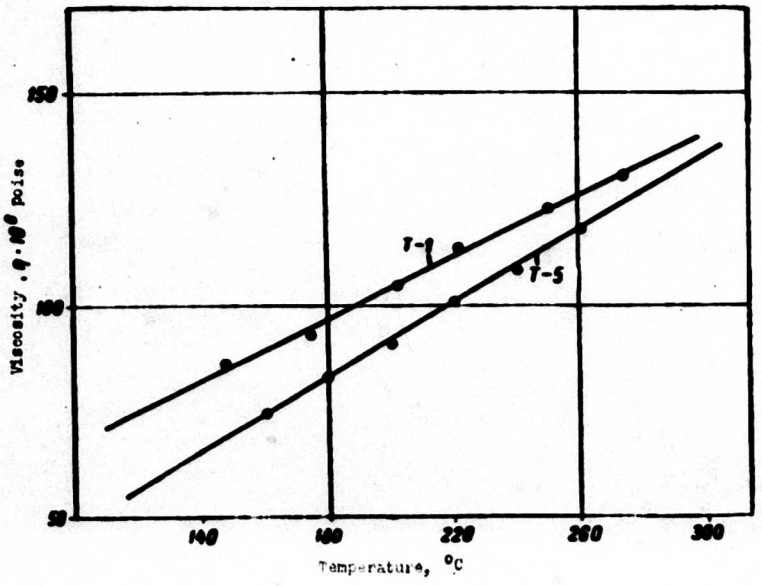

Fig. 8. Viscosity of vapors of fuels T-1 and T-5 at raised temperatures.

As can be seen from Fig. 8, the viscosity of the vapors of fuels T-1 and T-5 increases with an increase in temperature. The dependence of the viscosity of the vapors of the fuels on temperature is characterized by the following equation [25]:

$$\eta = 10^{-6} at^n$$

where η is dynamic viscosity, poise; a, n are constants; t is temperature, °C.

The constants a and n of the equation $\eta = 10^{-6} at^n$ are determined by the experimental curves (Fig. 8) and are equal, respectively, to 7800 and 1.54 for fuel T-1 and 9638 and 2.22 for fuel T-5.

Heat Capacity

Fig. 9 gives data on the heat capacity of the fuels T-5 and T-1 in the liquid state at temperatures of +20 to +280°C [2]. Heat capacity of fuel was determined by the method of direct heating. As can be seen from the given data, the heat capacity of fuels T-1 and T-5 at normal conditions (+20°C) is equal to 0.46-0.48 kcal/kg·deg and increases considerably with an increase in temperature. With lowering of temperature of boiling out of fuels their heat capacity increases somewhat (Fig. 9) and with an increase of temperature the distinction between heat capacities of fuels T-5 and T-1 increases. With an increase in the ratio C/H and also with increased branching of the hydrocarbons entering into the composition of jet fuels, heat capacity decreases. Thus alkane hydrocarbons of normal structure have the highest heat capacity [65-69].

The heat capacity of jet fuels at a temperature of 0°C can be calculated by the formula [52]

$$c_0 = \frac{A}{\sqrt{\rho_4^{15}}}.$$

For fuels the coefficient A should be taken equal to 0.403 [53]. The formula has been checked experimentally and can be used for jet fuels at temperatures from 0 to 400°C. The computed values differ from experimental data by no more than 4%. For calculation of the average heat capacity of liquid jet fuels we use equation [52]

$$c_{p_{av}} = c_0(1 + \alpha t),$$

where α is a coefficient, at temperatures from 0 to 200°C it is taken equal to 0.001;

t is temperature, °C;

C_0 is the heat capacity at 0°C and pressure 1 atm (tech.), kcal/kg·deg.

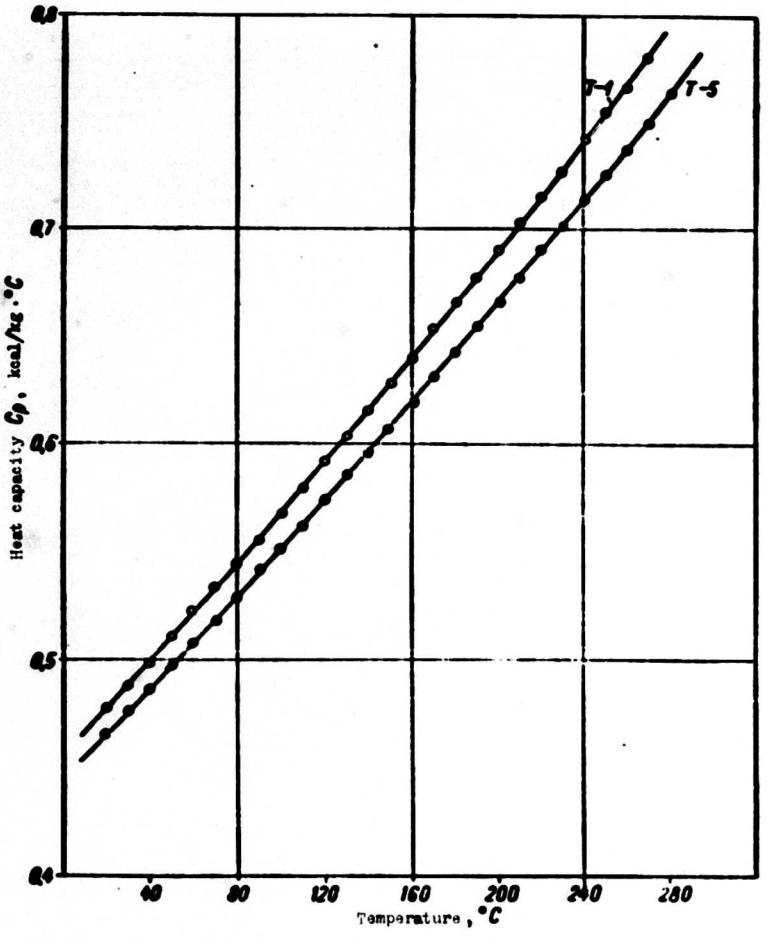

Fig. 9. Dependence of heat capacity of liquid fuels T-1 and T-5 on temperature.

Heat capacity of fuels in the liquid state depends on external pressure. With an increase in external pressure heat capacity decreases, although this decrease is small (Fig. 10). Thus, with an increase in pressure to 100 atm the heat capacity of fuel T-1 decreases, on the average, by 5-6%.

At high temperatures heat capacity decreases more sharply with an increase in pressure.

Figure 11 gives data on the heat capacity of vapors of fractions of fuels T-1 and T-5 [2]. On the basis of these data the average heat capacity of vapors of the fuels was determined.

As can be seen from Fig. 11, with an increase in temperature the heat capacity of vapors of the fuels increases. With a decrease in molecular weight of jet fuels the heat capacity of their vapors also increases.

For determination of average heat capacity of vapors of jet fuels at

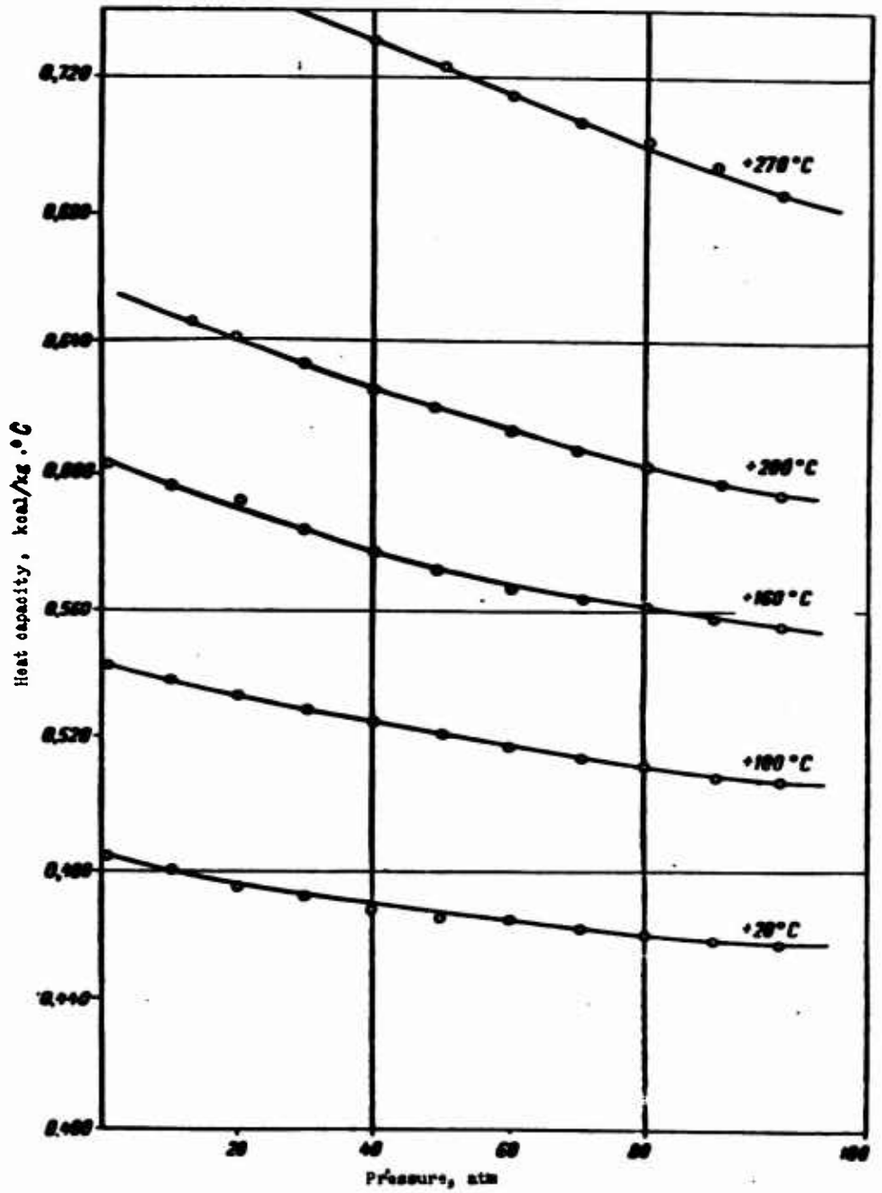

Fig. 10. Influence of pressure on heat capacity of fuel T-1 at various temperatures.

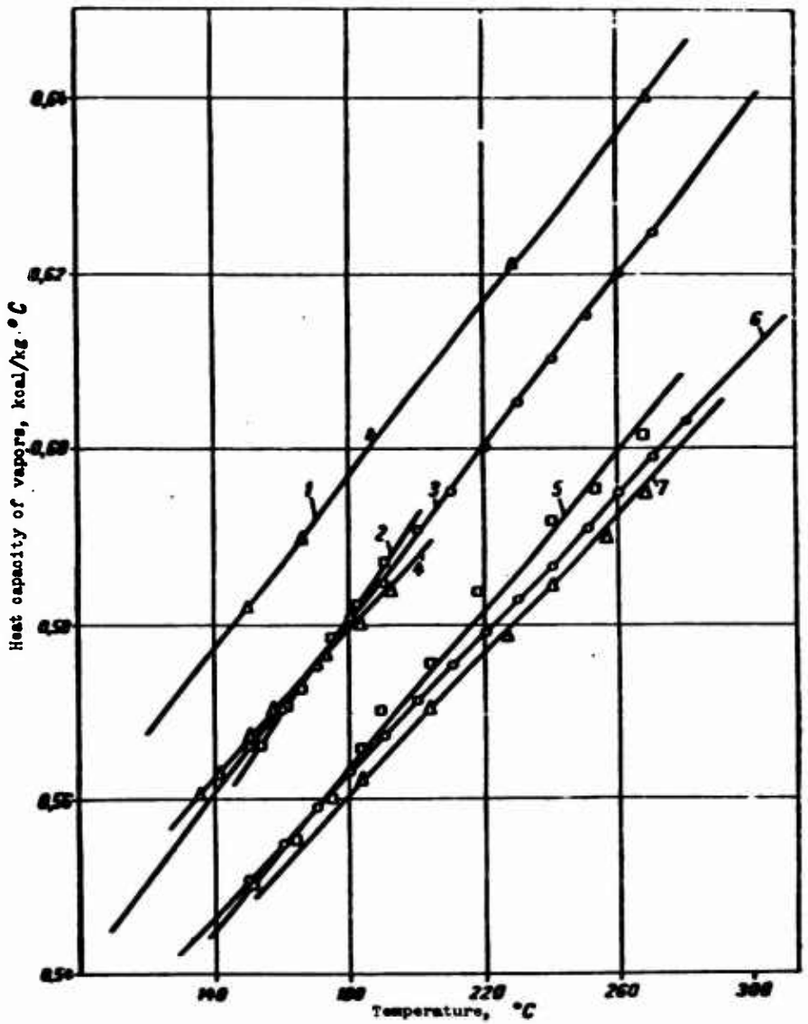

Fig. 11. Heat capacity of vapors of jet fuels and their fractions at various temperatures. 1 — fraction of T-1, 117-160°C; 2 — fraction of T-1, 160-170°C; 3 — fuel T-1; 4 — fraction of T-1, 170-200°C; 5 — fraction of T-5, 222-250°C; 6 — fuel T-5; 7 — fraction of T-5, 250-284°C.

temperatures of 0 to 300°C, use the following equation [52]:

$$C_p^m = C_p^0(1 + \alpha t),$$

where C_p^m is the average specific heat capacity per unit weight at constant pressure and temperature t, kcal/kg·deg;

C_p^0 is the average specific heat capacity per unit weight at constant pressure and a temperature of 0°C, kcal/kg·deg;

α is a coefficient for jet fuels, equal to 0.0012;

t is temperature, °C.

Thermal Conductivity

Thermal conductivity of propellants in the liquid phase depends on the temperature and chemical composition of fuels [2, 27, 28, 29].

With an increase in temperature the coefficient of thermal conductivity increases, this decrease occurs more noticeably for fuels evaporating at lower temperatures (Fig. 12).

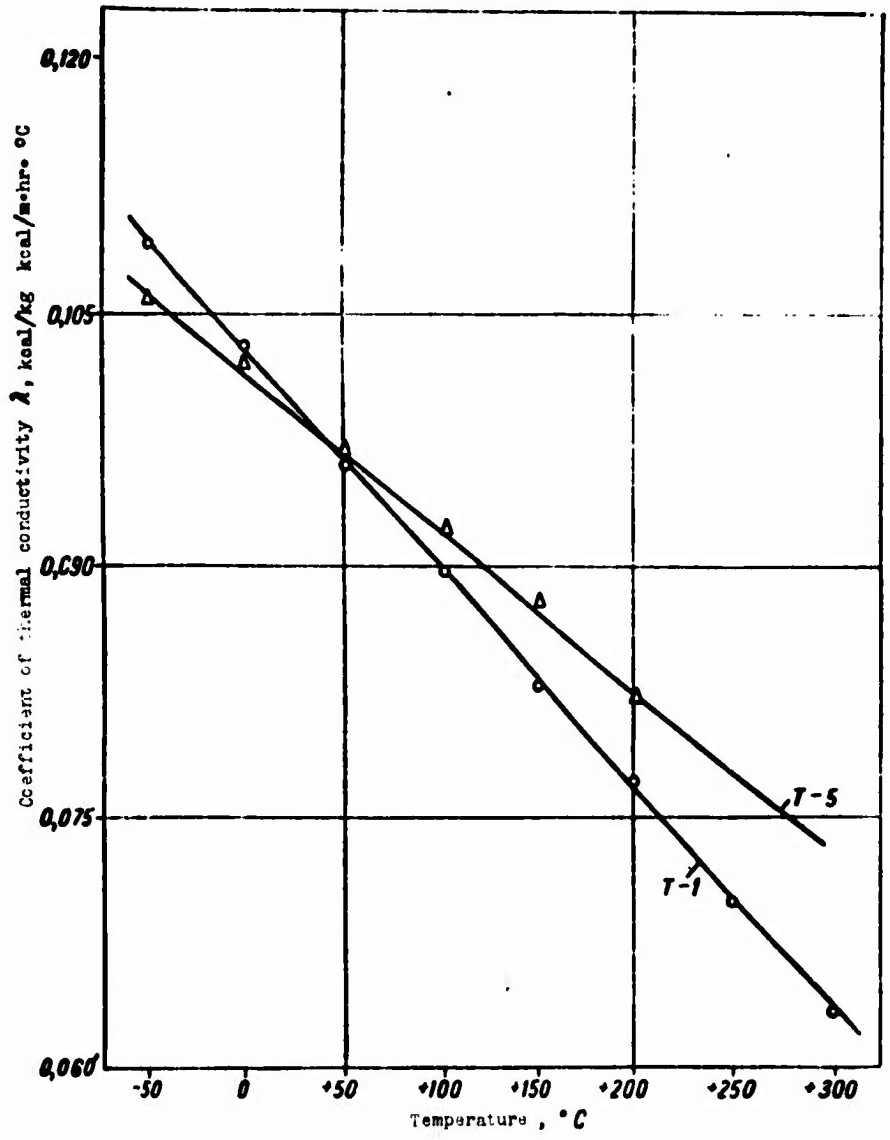

Fig. 12. Effect of temperature on coefficient of thermal conductivity of jet fuels in the liquid phase.

Pressure has an insignificant effect on the coefficient of thermal conductivity. With an increase in pressure of 1 to 20 atm (abs), the coefficient of thermal conductivity increases at temperatures up to +200°C on the average by 0.5% and with a further increase of temperature to 300°C, by 1%.

The thermal conductivity of vapors of jet fuels is considerably less than that of fuels in the liquid phase [2, 30, 31, 32]. The molecular weight of jet fuels in the vapor phase depends upon the temperature of the liquid phase; therefore the investigation of the thermal conductivity of vapors of fuels is connected with certain difficulties. It is somewhat easier to study the thermal conductivity of vapors of narrow fractions of fuels, inasmuch as their composition is more uniform than that of the vapors of the parent fuels.

Figure 13 gives data on the thermal conductivity of vapor of jet fuels and their fractions [2].

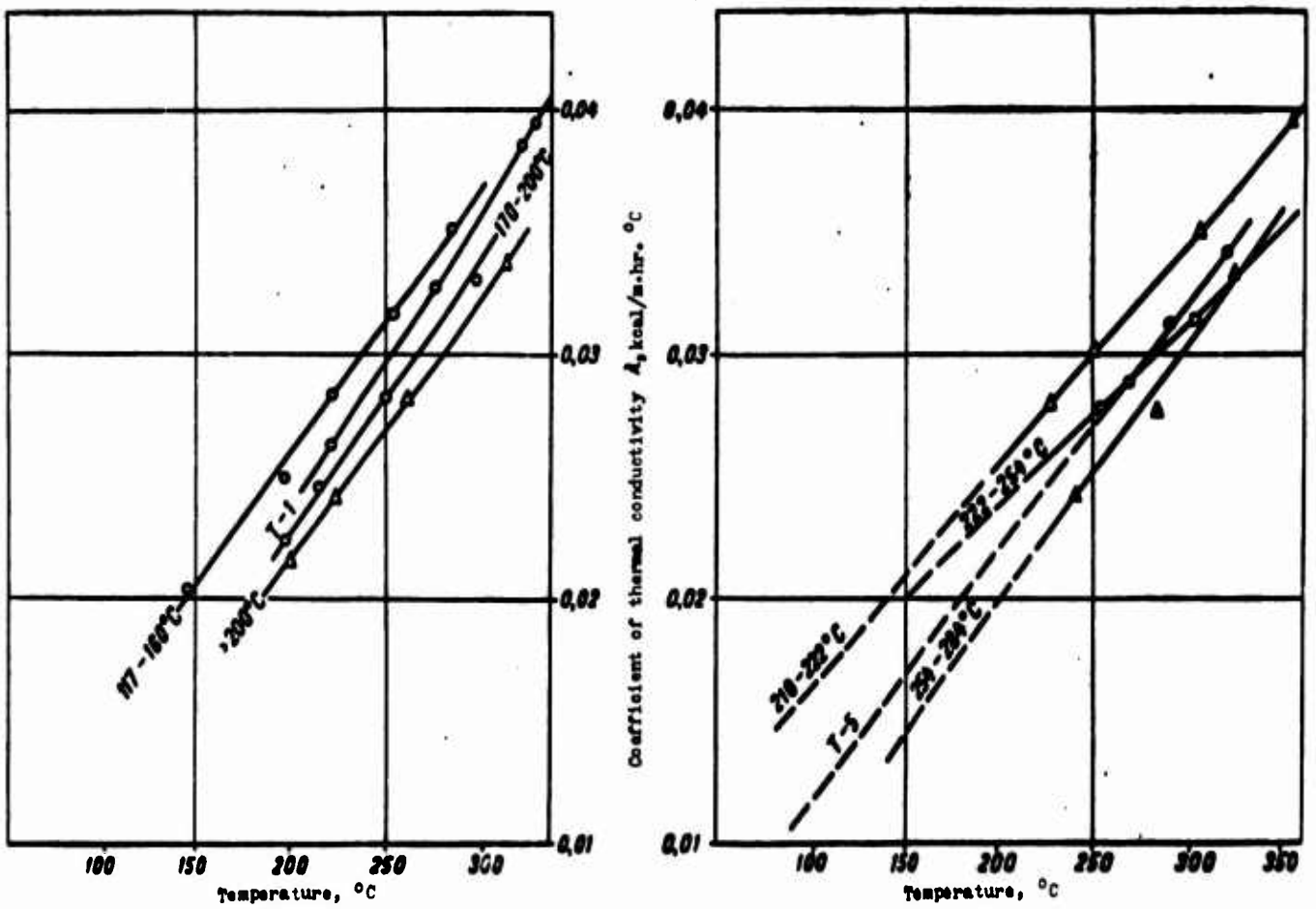

Fig. 13. Influence of temperature on thermal conductivity of vapors of fuels T-5 and T-1 and their fractions.

From the given data one can see that the coefficient of thermal conductivity of vapors of the fuels T-1 and T-5 decreases with an increase in the molecular weight of their hydrocarbon components. Independently of the molecular weight of

hydrocarbons in the vapors, the coefficient of thermal conductivity is also increased with a temperature increase. This is confirmed by other data [30, 59].

The dependence of the coefficient of thermal conductivity on temperature can be described by the equation of N. B. Vargaftik [29]

$$\lambda = \lambda_0 \left(\frac{T}{T_0}\right)^n,$$

where λ_0 is the coefficient of thermal conductivity at $T_0 = 273^\circ K$;

λ is the coefficient of thermal conductivity at T, $^\circ K$;

n is an exponent dependent upon the physicochemical nature of the fuel.

The values of n and λ_0 are given in Table 13.

Table 13. Values of n and λ_0 for Vapors of Fuel T-1 and Its Fractions [2]

Fuel T-1 and its fractions	λ_0, kcal/m·hr·°C	n
Parent fuel T-1	0.00740	2.05
Fractions of fuel T-1 boiling within the limits °C:		
117–160	0.00832	2.01
170–200	0.00725	2.07
more than 200	0.00676	2.08

For fuels T-2 and T-5, respectively, λ_0 is taken as 0.0088 and 0.00[illegible] and n as 2.00 and 2.10.

The coefficient of thermal conductivity of jet fuels at temperatures of 0 to 200°C can be calculated according to the following equation:

$$\lambda = \lambda_0 (1 - 0{,}0011\, t).$$

The error during determinations of λ by this equation constitutes about 10% [52].

For calculation of the coefficient of thermal conductivity at a pressure of 1.033 kg/cm^2 and a temperature of 0°C the following formula [53] is used:

$$\lambda_0 = \frac{0{,}101}{\rho_4^{15}},$$

where ρ_4^{15} is the density of fuel at 15°C, g/cm^3.

Besides this, the coefficient of thermal conductivity of vapors λ_0 at 0°C can be calculated by the formula [2]

$$\lambda_0 = 0{,}0114 - 0{,}0000224\, t_{\text{ср. хим}},$$

[ср.хим = av.b.p. = average boiling point]

where $t_{\text{av.b.p.}}$ is the average boiling point of fuels or their fractions.

It is not always possible to determine thermal conduction of fuels experimentally; therefore it is interesting to consider certain data on the calculation of the

coefficient of thermal conductivity. Of the greatest practical interest for the calculation of the coefficient of thermal conductivity is the equation [33]

$$\lambda_t = kA_0C_p\gamma_t^{4/3}M^{-1/3} \text{ kcal/m·hr·deg}$$

where $A_0 = 1.54$ is a universal quantity for all liquids at $T = 1/2\ T_{crit}$ °K;

γ_t is density, g/cm^3;

M is molecular weight;

C_p is the heat capacity at $T = (1/2)T_{crit}$ °K, kcal/g·deg;

T_{crit} is the critical temperature, °K;

k is a coefficient.

It has been established [33] that for a given fuel $A_0C_pM^{-1/3} = B$ is a constant quantity and does not depend on temperature. Thus, for jet fuels

$$\lambda = B\sqrt[3]{\gamma_t^4}.$$

If the density of fuels at different temperatures is known, then by the given equation one can also determine the thermal conductivity of fuels at different temperatures. The equation has been checked on many hydrocarbons [2, 35, 36, 37] and has shown satisfactory convergence with experimental data.

Values of coefficient B for fuels T-1 and T-5 constitute, respectively, 0.128 and 0.125 [2].

Heat of Evaporation

The heat of evaporation of jet fuels depends on their chemical and fractional compositions [2] and also on external pressure [52].

Table 14 gives data on the heat of evaporation of fuels T-1 and T-5 in an infinite volume.

Table 14. Heat of Evaporation of Fuels and Their Fractions at Various Temperatures

Designations of fuels and their fractions	Temperature Range, °C	Heat of evaporation		
		Molar kcal/mole	By unit weight kcal/kg	Volume kcal/liter
T-5	180—250	10200	56.2	47.3
T-1	20—50	9880	68.7	51.8
Fraction of T-1, °C:				
117—160	50—150	9200	67.0	—
170—200	100—200	9100	64.0	—
over 200	140—200	9070	58.3	—

As can be seen from the given data, the weight and volume heats of evaporation of fuels increase and the molar heat of evaporation decreases with a decrease in

the molecular weight of the constituent hydrocarbons and, consequently, also with lightening of the fractional composition.

At identical molecular weights of hydrocarbons, the heat of evaporation decreases with the transition from aromatic hydrocarbons to cyclanes, alkanes, and olefins. The smallest and approximately equal values of the heat of evaporation are found in alkanes and olefins.

In one homologous series, hydrocarbons with chains of isomeric structure have heats of evaporation lower than those of hydrocarbons with chains of normal structure; maximum difference can attain 5-10 kcal/kg.

The heat of evaporation is proportional to the average boiling point of fuels:

$$L = K\frac{T_{cp}}{M},$$

where L is the heat of evaporation, kcal/kg;

M is molecular weight;

T_{av} is average boiling point, ^{o}K.

The proportionality factor K is calculated according to one of the following equations [65]:

$$K = 8{,}75 + 4{,}571 \lg T_{cp};$$

or

$$K = 19{,}2 + 0{,}01 M.$$

For calculation of the heat of evaporation it is [illegible] Clausius-Clapeyron equation [2]:

$$\frac{dp}{dt} = \frac{AL}{T(V_n - V_m)},$$

where p is the pressure of saturated vapor, atm (tech.) T is absolute temperature, ^{o}K; L is molar heat of evaporation, kcal/mole; V_{vap} and V_{liq} are the specific volumes of vapor and liquid, m^3; A is a mechanical equivalent of heat.

The volume of liquid is usually disregarded and the volume of vapor is calculated by the formula

$$V_n = \frac{RT}{p}.$$

Integration of the equation leads to the relationship

$$\ln p = -\frac{AL}{RT} + C.$$

One can determine the molar heat of evaporation by the graphic dependence of ln p on 1/T.

Surface Tension

Surface tension of jet fuels is determined mainly by temperature and depends also on the chemical and fractional compositions [2, 38, 39]. Figure 14 shows the dependence of surface tension of fuels T-5 and T-1 on temperature. Measurements of surface tension of fuels at temperatures above their boiling points were produced under increased pressure. With an increase of temperature from -40 to +300°C the surface tension decreases by 4-6 times. This occurs because with the increase in temperature the bonds between molecules of fuel are weakened; at critical temperature the surface tension of the fuels becomes equal to zero. With an increase in the temperature of boiling away of fuels their surface tension increases.

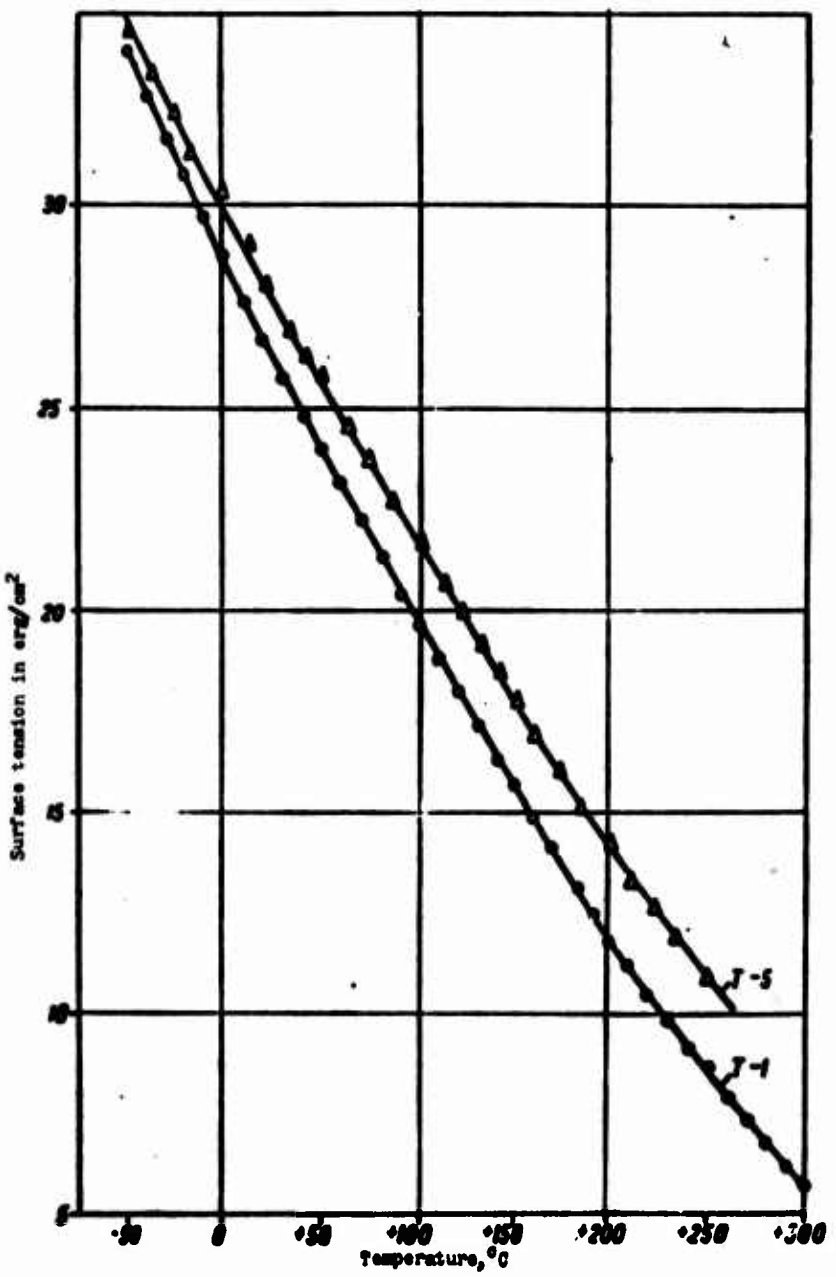

Fig. 14. Influence of temperature on surface tension of jet fuels.

At a temperature of 20°C hydrocarbons of jet fuels evaporating within the limits 65-300°C have the following surface tension (erg/cm^2): paraffin (18-28)·10^{-3}; napthenic (29-32)·10^{-3}; and aromatic (28-32)·10^{-3} [39, 58].

The derivation of empirical equations for the calculation of surface tension of fuels is complicated by the fact that the fuels are multicomponent mixtures, the composition of whose vapor and liquid phases changes strongly with temperature.

Several equations for the calculation of surface tension of fuels are known which give good convergence with experimental data [2-38, 40, 52-56].

With changes of temperature of liquid fuels in a wide interval the surface tension can be calculated by the formula [53]

$$\sigma = \sigma_0 \frac{T_{кр} - T}{T_{кр} - T_0},$$

[кр = crit = critical]

where T_{crit} is critical temperature, °K;

T is temperature, °K

T_0 is 273°K;

σ is surface tension, kg/cm^2;

σ_0 is surface tension at 0°C and p = 1.033 kg/cm^2.

At temperatures from -30 to +100°C, surface tension can be calculated by the formula [39, 52, 55]

$$\sigma = \sigma_0 - \alpha t,$$

where $\alpha \approx 10^{-4}$; t is temperature, °C.

For calculation of the surface tension of fuels T-1, TS-1, and T-5 it is possible to use Van der Waals equations:

$$\sigma = \sigma_0 (T_{кр} - T)^n,$$

where σ_0 and n are constants, characteristic for every fuel.

Surface tension of fuels T-1 and TS-1 can be calculated by the equation

$$\sigma = 8{,}99 \cdot 10^{-4} (510 - t)^{1.736},$$

and surface tension of fuel T-5 by the equation

$$\sigma = 6{,}44 \cdot 10^{-3} (470 - t)^{1.375}.$$

These equations are useful for calculation in the temperature interval from -50 to +300°C.

Besides this surface tension of fuel T-5 can be calculated also by the equation [38, 55]

$$\sigma = 618\,\nu^{3} \cdot 10^{-2.0915\,\nu},$$

where ν is kinematic viscosity, cs.

The equation is useful for calculation of surface tension at temperatures of -40 to +300°C.

There is also known an equation connecting the surface tension of fuels with their density [52]:

$$\sigma = \frac{5\rho_4^{20} - 1{,}5}{100}.$$

The equation agrees satisfactorily with experimental data [52-54].

Coefficient of Diffusion

The diffusion of vapors of jet fuels in air has been comparatively little studied. There are only a few works dedicated to the study of the coefficient of diffusion of vapors of fuel [2, 52, 59, 72-75].

Process of diffusion is described by Fick's equation

$$dG = -D\frac{dC}{dx}\,dS\,d\tau,$$

where dG is the quantity of matter passed in time $d\tau$ through surface dS, $kg/m^2 \cdot sec$;

C is the concentration of vapors, kg/m^3;

x is a coordinate, perpendicular to the translation surface, m;

D is the coefficient of diffusion, usually expressed in m^2/sec.

Several empirical formulas for calculation of the coefficient of diffusion D are known; the most satisfactory results can be obtained with help of the following equation [71]:

$$D_0 = A\frac{\sqrt{\frac{1}{M_{vap}} + \frac{1}{M_{air}}}}{\left(\sqrt[3]{V_{vap}} + \sqrt[3]{V_{air}}\right)^2} - B,$$

[в = air]

where M_{air} is the molecular weight of air, equal to 28.97;

M_{vap} is the molecular weight of the vapor of the fuel;

V_{air} is the molar volume of air;

V_{vap} is the molar volume of fuel vapor;

V_{vap} is calculated by the formula [71].

$$V_{vap} = 14{,}8n + 3{,}7m + 21{,}2k,$$

where n, m, k are the numbers of atoms of carbon, hydrogen, and oxygen, respectively, in an "average" molecule of fuel;

A, B are constants, selected experimentally.

The coefficient of diffusion depends on the temperature and pressure of the medium. This dependence is described by the following equation [52, 59]:

$$D = D_0 \left(\frac{T}{T_0}\right)^m \frac{p_0}{p},$$

where m = 1.5-2.0.

In a small interval of temperatures the change of the coefficient of diffusion with temperature can be taken as linear [72, 73].

Several methods are known for experimental determination of the coefficient of diffusion [2, 70]. Using the Frank-Kamenetskiy method, Yu. D. Vasilevskaya [2] determined the diffusion of vapor of fuel T-5 and its fractions in air (Table 15).

Table 15. Influence of Temperature on the Coefficient of Diffusion (cm^2/sec) of Vapors of Fuel T-5 and its Fractions at a Constant Pressure of 760 mm Hg

Temperature, °C	1 fraction 197-228°C (average molecular weight 167)	2 fraction 228-242°C (average molecular weight 184)	3 fraction 242-255°C (average molecular weight 193)	4 fraction 255-301°C (average molecular weight 209)	Fuel T-5
0	0,0333	0,0303	0,0282	0,0265	0,0287
250	0,1146	0,1070	0,1015	0,0973	0,1026
260	0,1186	0,1109	0,1053	0,1009	0,1064
270	0,1229	0,1149	0,1092	0,1047	0,1104
280	0,1273	0,1191	0,1132	0,1087	0,1144
290	0,1316	0,1233	0,1173	0,1126	0,1184
300	0,1362	0,1277	0,1215	0,1168	0,1224
310	0,1407	0,1319	0,1259	0,1208	0,1269
320	0,1454	0,1365	0,1300	0,1251	0,1313
330	0,1500	0,1410	0,1343	0,1290	0,1356
340	0,1548	0,1454	0,1385	0,1336	0,1400
350	0,1597	0,1502	0,1433	0,1380	0,1445
360	0,1645	0,1548	0,1477	0,1423	0,1491
370	0,1695	0,1596	0,1524	0,1470	0,1538
380	0,1746	0,1646	0,1572	0,1517	0,1586
390	0,1796	0,1693	0,1618	0,1562	0,1633
400	0,1848	0,1744	0,1668	0,1610	0,1683

As can be seen from Table 15, the coefficient of diffusion decreases with an increase in the molecular weight of hydrocarbons and increases considerably with an increase in temperature.

At identical molecular weights, the highest coefficients of diffusion are found in cyclane hydrocarbons and the lowest in aromatic hydrocarbons. Alkane hydrocarbons occupy an intermediate position. It is necessary to note that the difference in coefficients of diffusion of vapors of different hydrocarbons decreases with a growth in molecular weight.

Hygroscopicity

The hygroscopicity of jet fuels depends on external conditions (atmospheric humidity, pressure, temperature) and on the chemical composition of the fuels.

The solubility of water in fuels is directly proportional to atmospheric humidity [5, 45-49]. Figure 15 shows the dependence of the water content in kerosene on atmospheric humidity. The humidity of atmospheric air constantly changes; therefore the content of water in fuels changes. Water dissolved in fuel is in constant equilibrium with the moisture of atmospheric air. With an increase in atmospheric humidity the content of water in the fuel is increased; with a decrease in humidity, it decreases. The solubility of water in fuels is essentially influenced also by temperature. Other things being equal, with an increase in temperature the solubility of water in jet fuels increases; with a decrease in temperature, it decreases (Fig. 16). However, the content of water in fuels depends not only on the absolute value of temperature, but also on the difference of the temperatures of the fuel and the air.

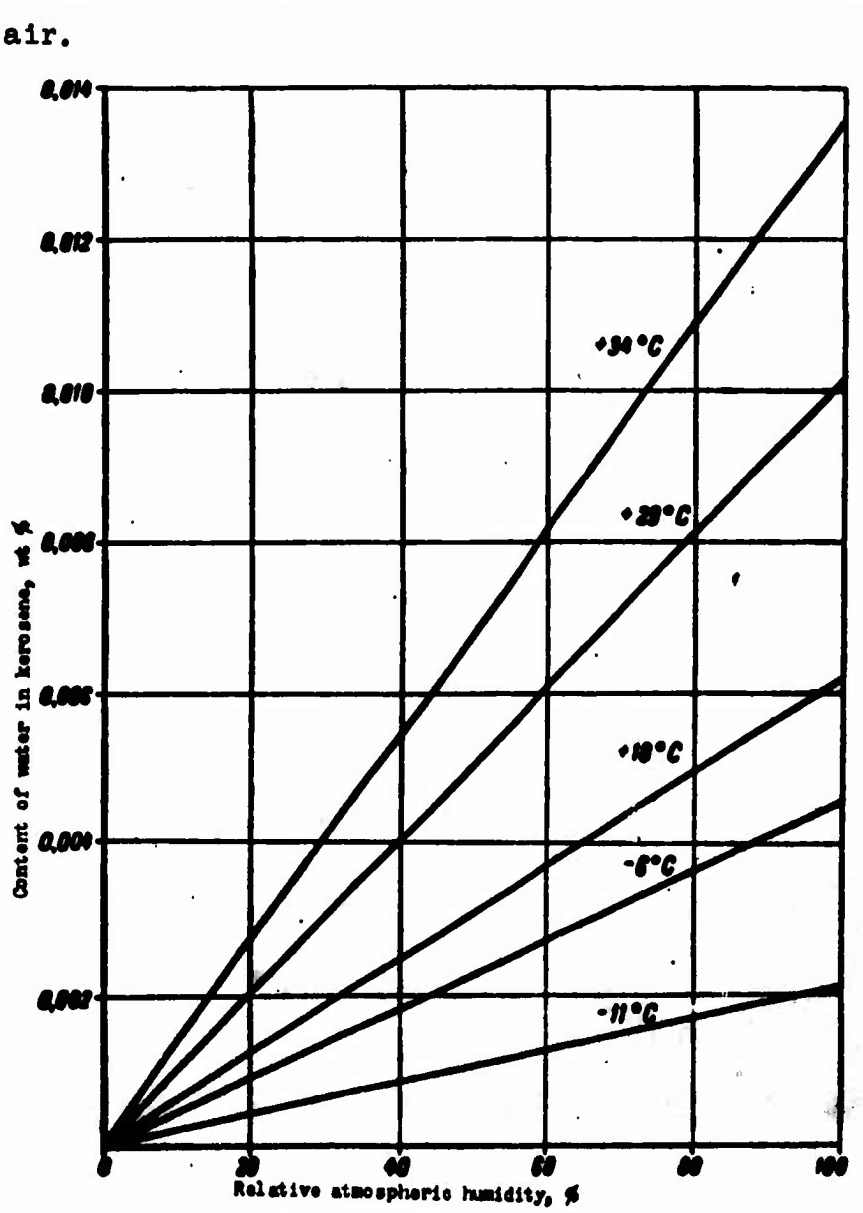

Fig. 15. Influence of relative atmospheric humidity on the solubility of water in kerosene.

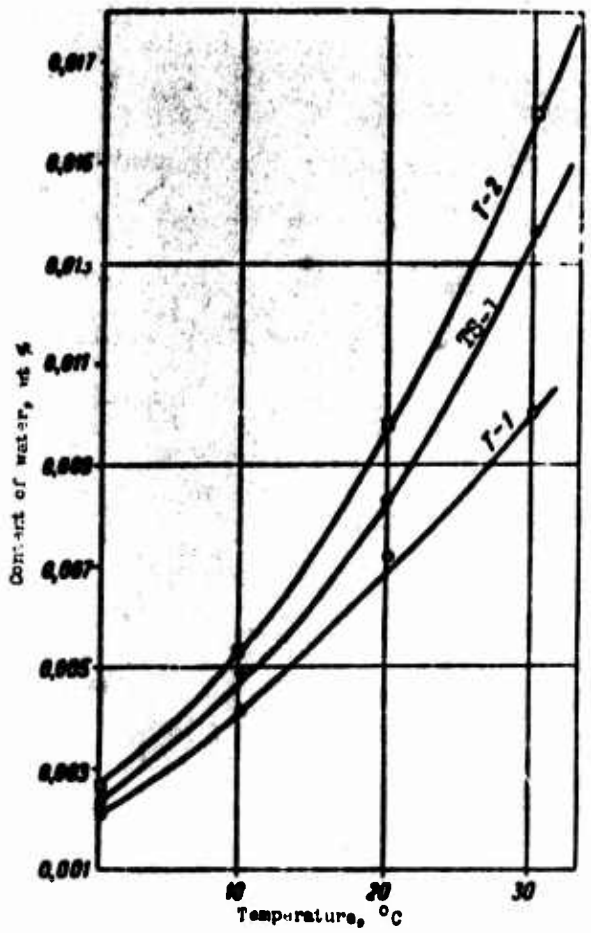

Fig. 16. Solubility of water in jet fuels at various temperatures.

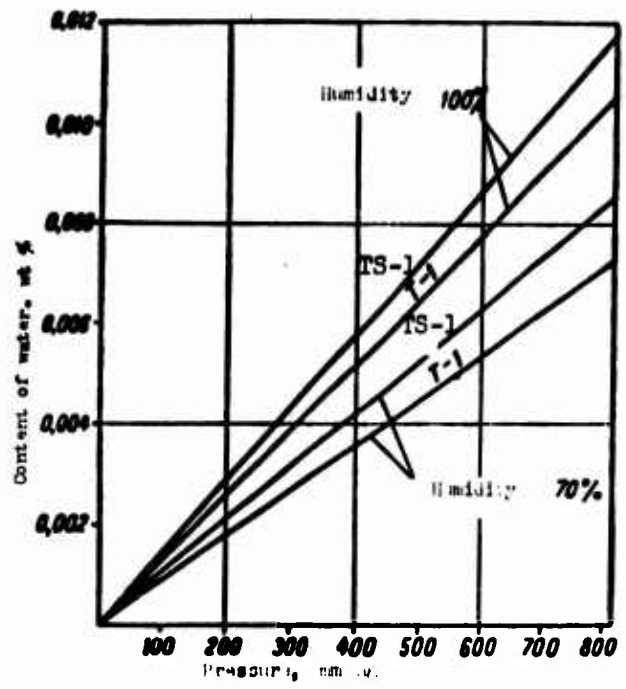

Fig. 17. Influence of atmospheric pressure on the solubility of water in jet fuels.

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With a decrease in external pressure (for in tar imbs) the content of water dissolved in the fuel decreas [illegible] the content of water in fuel with a decrease in external pressure occurs more intensely in air with reduced relative humidity (Fig. 17).

The speed of saturation of jet fuels by water is sufficiently great and depends on the relative atmospheric humidity of the area of contact of the fuel with the air, on the thickness of the fuel layer, and on certain other factors (Fig. 18). Saturation of fuel by water occurs especially intensely in the first minutes. It is necessary to note that at corresponding temperature conditions the speed of absorption of water by fuel from aqueous sediment is considerably less than that from the atmosphere. This is explained [5] by the fact that molecules of water in the liquid phase are united in groups. Therefore the transfer of water from the blanket into the fuel will be connected with the expenditure of a certain quantity of energy on the breaking of molecular bonds. This has been confirmed by experimental data (Fig. 18).

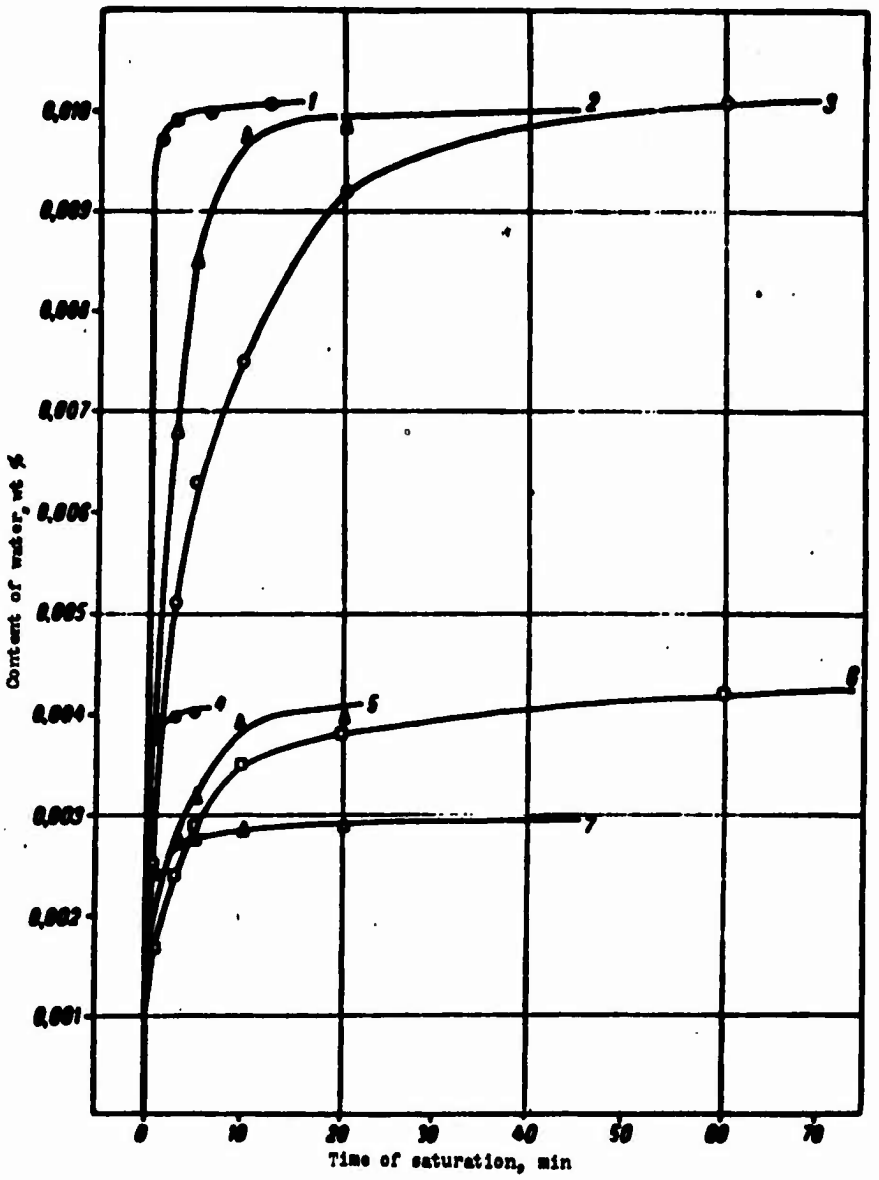

Fig. 18. Rate of saturation of dry TS-1 fuel by water from air and from a water blanket at a temperature of 17-18°C. 1-3 – saturation from air at a relative humidity of 95%; 4-6 – saturation from air at a relative humidity of 30%; 7 – saturation from water blanket.

The solubility of water in jet fuels depends on their chemical composition and molecular weight [3, 7, 49, 60-64].

In terms of hygroscopicity, hydrocarbons are arranged in the following ascending series: alkanes-alkenes-cyclanes-aromatic hydrocarbons.

Independently of the chemical structure of the hydrocarbons entering into the composition of the fuels, their hygroscopicity decreases with an increase in molecular weight. Thus the hygroscopicity of fuel T-2 is higher than that of fuels T-1, TS-1, and (especially) T-5.

Table 16 gives average data on the content of water in jet fuels in constituent hydrocarbon groups.

Table 16. Hygroscopicity of Propellants and Hydrocarbon Groups [7]

Fuels and hydrocarbon groups	Hydrocarbon composition, wt %				Content of water, wt %
	Aromatic	Alkene	Cyclane	Alkane	
TS-1	18,7	2,2	19,8	59,3	0,010
T-1	19,5	2,0	45,0	33,5	0,008
T-2	19,6	1,7	21,6	57,1	0,012
T-5	20,6	0,7	57,0	21,7	0,005
Alkane-cyclane fraction					
TS-1	0	0	22,0	78,0	0,002
T-1	0	0	59,0	41,0	0,001
T-2	0	0	28,0	72,0	0,002
T-5	0	0	51,4	48,6	0,001
Aromatic fraction					
TS-1	97,8	0,1	1,2	0,9	0,031
T-1	98,1	0,6	0,3	1,0	0,030
T-2	95,3	2,1	0,8	1,8	0,036
T-5	98,0	1,0	1,0	—	0,027

With an increase in the content of aromatic hydrocarbons, the hygroscopicity of fuels is increased (Table 17).

Table 17. Influence of Aromatic Hydrocarbons on Hygroscopicity of fuels TS-1 and T-1 [7]

Quantity of aromatic hydrocarbons added to alkane-cyclane fractions	Content of water, wt	
	T-1	TS-1
10	0,006	0,006
20	0,008	0,010
30	0,011	0,012
60	0,019	0,021

Solubility of water in hydrocarbons (C) of jet fuels can be expressed by the equation [5]

$$\lg C = \lg C_1 \frac{b}{t},$$

where C_1 is the content of water in the parent fuel, wt. %;

b is a coefficient dependent on the chemical nature of fuel;

t is temperature, ^{o}C.

If fuel is heated it becomes completely saturated by moisture. After the achievement of an equilibrium state corresponding to the established temperature the process stops. In case of high atmospheric humidity the process continues with simultaneous transfer of excess moisture from the fuel into sediment.

During cooling the fuel returns its moisture to the atmosphere ("dries"). At a temperature below zero the moisture emanated from fuel will freeze in the space above the fuel in the reservoir and will fall into the fuel in the form of crystals of ice. With a sharp lowering of the temperature of the fuel to negative values, the moisture emanated from the depth of the fuel, not reaching the external air, will freeze. In this case floating crystals of ice in the form of the finest needles of hoarfrost will be observed throughout the entire depth of the fuel.

In connection with the constantly varying atmospheric conditions, the processes of saturation of fuel by moisture, of its accumulation in sediment, of the separation from the fuel of moisture, and the formation of crystals of ice are extremely dynamic and proceed in the entire period of storage of the fuel or of its stay in the tanks of an aircraft.

Solubility of Air

Air dissolved in the fuel negatively affects certain operational properties of fuels (in the first place, their pumping quality at great heights) and dissolved oxygen contained in the fuel is a cause of the development of processes of oxidation of the least stable components of fuels.

The solubility of air in jet fuels is uneven and depends on the molecular weight of the constituent hydrocarbons, density, viscosity, surface tension, and also the content of water in fuels.

With an increase in the molecular weight of hydrocarbons of fuels the solubility of air in them decreases. The influence of density, viscosity, and surface tension on the solubility of air in fuels is shown in Table 18.

Table 18. Solubility of Air in Various Fuels

Fuel properties at 21°C			Solubility of air at 21°C and 760 mm Hg, vol %
Surface tension dynes/cm	Viscosity, cs	Density, g/cm³	
28,3	898	0,885	7,75
26,5	388	0,850	9,05
25,8	17,5	0,870	8,70
23,4	1,7	0,780	17,20
18,4	0,6	0,723	22,80

With a decrease in external pressure, the solubility of air in fuels decreases and air dissolved in the fuel starts to be liberated, taking fuel vapors with it. The solubility in jet fuels of oxygen, nitrogen, carbon dioxide, and the other

components of air is uneven. Oxygen has the greatest solubility. For instance, at +15.5°C the coefficient of solubility of oxygen in fuels of type T-1 and TS-1 is equal to 0.0285, and that of nitrogen to 0.0157. Therefore the gas mixture liberated from fuel during a change in external conditions contains almost 2 times more oxygen than ordinary air [76].

In fuels with a raised content of moisture the solubility of air is somewhat increased. Therefore in conditions of lowered pressure quantity of gases emanated from flooded fuels is greater than that from "dry" fuels.

Molecular Weight

The "average" molecular weight of jet fuels depends on their fractional and chemical compositions and is equal for the fuels T-2, TS-1, and T-1 to 135-150; for T-5 it is 190 [8].

The "average" molecular weight of jet fuels can be calculated by the following empirical formula [53]:

$$M = (7K - 21{,}5) + (0{,}76 - 0{,}04K)\,t_s + (0{,}0003K - 0{,}00245)\,t_s^2,$$

where $K = \frac{1.216\sqrt[3]{273 + t_s}}{\rho_{15}^{15}}$ is a factor characterizing the chemical composition of the fuels; K varies from 10 to 13; t_s is the average boiling point of the fuel, °C; ρ_{15}^{15} the density of the fuel, g/cm^3.

The divergences between experimental data and those calculated by the above-cited formula do not exceed 2%.

Accumulation of Static Electricity in Fuels

Propellants are good dielectrics. Their conductivity lies in the range from 10^{-11} to $1.5 \cdot 10^{-15}$ ohm^{-1}·cm^{-1} and their dielectric constants range from 2.07 to 2.14 [77]. If moving jet fuels touch solid bodies, static electricity appears. In conditions of storage, transportation, and application of jet fuels electric charges of various polarity are formed on the interface "fuel – solid body." Subsequently such charges can be stored in the fuel. With the achievement of a certain drop (critical) of electric field strength there appears an electrical charge which, in certain conditions, can lead to explosion or fire [78].

The critical magnitude for jet fuels is a magnitude of the order of 30 kv/cm. The quantity of electrical charges stored in a flow of jet fuels in a unit of time depends on the composition and concentration of different impurities – heteroorganic compounds with high polarity, solid particles (sand, insoluble precipitates, and

others), viscosity, density, and dielectric properties of the fuel. The rate of accumulation of electricity is affected also by the state of the internal surface of pipelines of fuel tanks and reservoirs, conditions of filtration, and speed of movement of the fuel.

The presence in jet fuels of water and dissolved gases intensifies the accumulation of static electricity.

Current (i) appearing as a result of this can be expressed by the following equation [79]:

$$i = -0{,}0395\,\pi\varepsilon\varepsilon_0 G v Re^{0.75},$$

where ε is the relative dielectric constant of the fuel;

ε_0 is the dielectric constant of a vacuum, $\varepsilon_0 = 8.854 \cdot 10^{-14}$;

G is the electrokinetic potential, volts;

v is the average speed of liquid, cm/sec;

Re is the Reynolds number.

Considering that

$$Re = \frac{vd}{\nu},$$

where d is the internal diameter of pipeline, and

ν is viscosity in cs;

it is possible to write

$$i = -0{,}0395\,\pi\varepsilon\varepsilon_0 G v^{1.75}\left(\frac{d}{\nu}\right)^{0.75}.$$

The magnitude of the appearing current is directly proportional to the speed of liquid and the diameter of a pipeline and is inversely proportional to viscosity. Thus, less viscous fuels are more inclined to accumulate static electricity.

The formula was subjected to an experimental check. On a laboratory installation jet fuel was pumped over pipelines of stainless steel [80]. An empirical dependence of the magnitude of the electrical current (i_e) on certain factors was obtained:

$$i_e = 8 \cdot 10^{-10} k \tau v^{1.75}\left(1 - e^{-\frac{L}{\tau v}}\right),$$

[э = e = electrical]

where k is a coefficient which depends on the diameter of the pipe and the conditions of separation of charges on the fuel – pipe boundary;

v is the average speed of pumping, m/sec;

L is the length of the pipeline, m;

τ is the relaxation time of the product, sec.

It was found that for a jet fuel with resistivity of about $2 \cdot 10^{13}$ ohm·cm, the quantity $k\tau = 2.15$.

During servicing of aircraft and pumping of fuel electrical charges appear which are gradually accumulated in reservoirs or fuel tanks. However, in connection with the conductivity of jet fuels (although very small) there occurs gradual leakage to the walls of the reservoir (fuel tank) and then, if they are metallic and are grounded, into the earth. In completely filled fuel tanks or reservoirs the leakage rate can be expressed thus:

$$dQ = -\frac{Q}{\tau} d\tau,$$

where Q is the quantity of charges existing in the liquid, k;

τ is relaxation time, sec.

The quantity of proceeding charges can be determined by the above-cited formulas, and relaxation time equals

$$\tau = \frac{\varepsilon\varepsilon_0}{\gamma},$$

where γ is conductivity of fuels, $ohm^{-1} \cdot cm^{-1}$.

Inasmuch as the dielectric constant of jet fuels is practically [illegible] and equals ~2, relaxation time is determined basically by conductivity, which varies in wide limits.

During servicing of aircraft with fuel they must be thoroughly grounded. It is necessary also reliably to ground reservoirs, pipelines, and pumping gear. This will, to a considerable degree, decrease the danger of accumulation of static electricity in fuels. However, the danger of accumulation of static electricity in flight remains. Especially dangerous are prolonged (more than 2-3 hr) flights in thunderstorm weather.

Cooling Capability

The specific heat flow (Φ_K) which is transmitted from the wall into jet fuels is determined by the equation

$$\Phi_K = \alpha_T (T_{cT} - T_T),$$

[T = f = fuel, cT = w = wall]

where α_f is the coefficient of convective heat exchange in cooling fuel, depending on the properties of the fuel, in $kcal/m^2 \cdot sec. {}^{\circ}K$;

T_w is the temperature of the cooled wall on its contact surface with the fuel, $^{\circ}K$;

T_f is the temperature of the fuel, $^{\circ}K$.

The process of heat exchange in the convective heat exchange region (up to T_w = 360°C) is described by the Mikheyev equation [81, 83]:

$$Nu = 0{,}021\, Re^{0.8} Pr^{0.43} \cdot \frac{Pr^{0.25}}{Pr_{cr}^{0.25}},$$

where Re, Pr are the Reynolds and Prandtl numbers for the fuel; Pr_w is the Prandtl number calculated for conditions of movement of fuel at the wall.

In work [82] the following dependence is given:

$$Nu = 0{,}027\, Re^{0.8} Pr^{0.33} \left(\frac{\eta_f}{\eta_{cr}}\right)^{0.14},$$

where η_f is the dynamic viscosity of the fuel, cp;

η_w is the dynamic viscosity of the fuel at the wall, cp.

The equation can also be written in the form

$$Nu = 0{,}027 \left(\frac{Dv\rho}{\eta_f}\right)^{0.8} \left(\frac{\eta_f C_p}{\lambda}\right)^{0.33} \frac{\lambda}{D} \left(\frac{\eta_f}{\eta_{cr}}\right)^{0.14},$$

where ρ is the density, kg/m^3;

v is the speed of the fuel, m/sec;

C_p is the specific heat capacity, kcal/kg·deg;

λ is the coefficient of thermal conductivity, kcal/m·hr·deg.

In this expression the magnitudes of viscosity, heat capacity, and thermal conductivity are usually calculated at average temperature of the boundary layer

$$T_s = \frac{T_{cr} + T_f}{2}.$$

The temperature of the beginning of thermal disintegration of jet fuels lies within the limits 340-380°C. In the region of unstable conditions of heat exchange (at T_w > 380°C) the following empirical formula is valid:

$$\Delta t = (4{,}52 - 0{,}629\, t_f^{\frac{1}{3}}) \cdot 10^{-3} \frac{q}{w} + B - t_f,$$

where Δt is the drop in temperatures, wall – fuel, °C;

t_f is the temperature of the fuel, °C;

q is the specific heat flow, kcal/m^2·hr;

w is the speed of flow of the liquid, m/sec;

B is an empirical coefficient, °K.

From the above, it follows that the best cooling properties will be found in fuels of high density, thermal conductivity, and specific heat capacity and lower viscosity.

Temperature Limits of Explosiveness of Vapors of Fuels in Air

Temperature limits of the explosiveness of jet-fuel vapors depend on the external

pressure, the chemical nature of the fuel, and certain other factors. With a decrease in external pressure, evaporation of fuels increases; therefore, with ascent of an aircraft to great altitudes explosive mixtures of fuel vapor with air can be formed at lower temperatures.

Figure 19 presents experimentally determined [84] temperature limits of explosiveness of mixtures of jet fuel vapors with air. Explosive zone of fuel T-1 at sea level lies within the limits 25-65°C. With lightening of fuels the temperature limits of explosiveness are expanded and at sea level for fuel TS-1 they have a value of +10 to +60°C. With a climb to altitude the temperature zone of explosiveness of all fuels is narrowed and shifted into a zone of lower temperatures (Fig. 19).

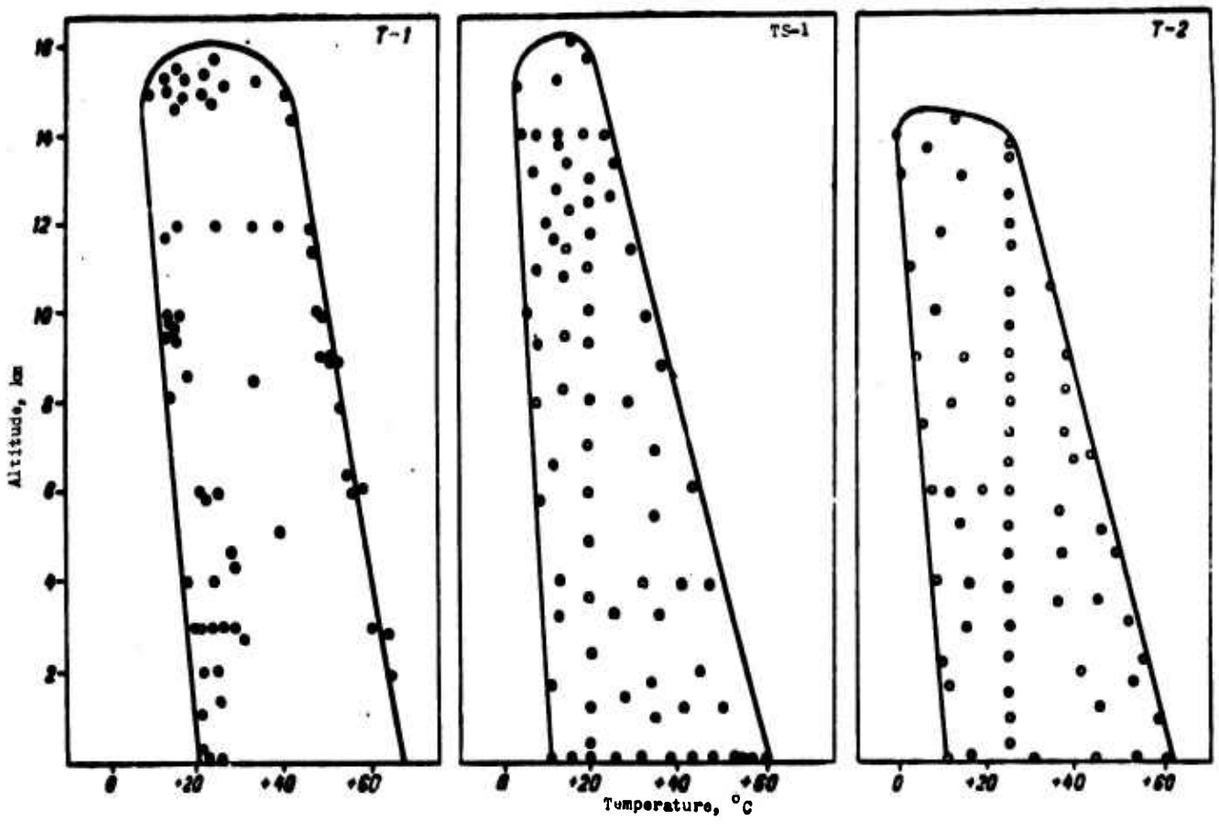

Fig. 19. Effect of altitude on the temperature limits of the formation of explosive mixtures of jet fuel vapors.

For every fuel, depending upon pressure of saturated vapors, there exists a certain limit of rarefaction above which strong evaporation of fuel, with formation of overenriched mixtures, sets in. Such mixtures ignite unstably. The altitude of the beginning of formation of overenriched mixtures for fuels TS-1 and T-1 is 15 km, and that for fuel T-2 is about 14 km. These zones are outlined in Fig. 19.

Flash Point and Self-Ignition

In operational conditions there can be cases of ignition of fuels outside the combustion chamber, caused by open fire and by heated surfaces. The inflammability of a fuel is characterized by the flash point and temperature of self-ignition; it depends on the chemical and fractional composition and also on external conditions. Flash points and self-ignition temperatures of jet fuels are given in Table 19.

Table 19. Flash Point and Temperature of Self-Ignition of Jet Fuels [84]

Fuels	Temperature, °C		
	flash in closed crucible	self-ignition*	heated plate provoking ignition of fuel
T-1	+30	220	325
TS-1	+28	248	325
T-1	−12	233	330

*Temperature of self-ignition was determined with injection of 0.2 ml of fuel onto a heated metallic surface; the temperature in the gas phase and of the metallic plate itself was measured.

With lightening of fuels the flash point is lowered and the temperature of self-ignition is increased. Thus, if fuels T-1, TS-1, T-2 and T-5 strike a metallic surface whose temperature is higher than 325°C their ignition is possible.

With a decrease in external pressure the temperature of self-ignition of fuels is increased (Table 20).

Table 20. Effect of Altitude on Temperature of Self-Ignition of Fuels [85]

Fuel	Temperature of self-ignition, °C	
	Pressure 742 mm Hg	Pressure 370 mm Hg
JP-1	226	402
JP-2	238	440
JP-3	242	444

External pressure also influences the flash point. With a reduction in external pressure increases pressure of saturated vapors increases and the flash points drops. An explosive mixture of fuel vapors with air can be formed at a vapor pressure as low as 8-10 mm Hg.

One of the methods of reducing the danger of explosion of jet-fuel vapors is the introduction of an inert gas into the vapor space of the fuel tanks.

Fire extinguishing concentrations in the vapor space are as follows (in wt. %): for CO_2, ~22; N_2, ~30.9; CH_3Br, ~40; CCl_4, 7.7. Halide derivatives of hydrocarbons have quite a high fire-extinguishing effect.

However, filling the vapor space with inert gas requires installation of additional equipment on the aircraft. It is considered that the weight of such equipment will be about 1.2% of the weight of loaded fuel.

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C H A P T E R III

CHEMICAL COMPOSITION OF JET FUELS

Commercial jet fuels consist of two unequal groups of compounds. The first, predominant, group includes hydrocarbons and the second, nonhydrocarbon impurities. Among the hydrocarbons present are alkane structures of chiefly isomeric structure, cyclanes and aromatics, mainly monocyclic with side chains. The quantity of polycyclic aromatic hydrocarbons in fuels does not exceed 3%. Alkane hydrocarbons are present in fuels in amounts of 33-61%, and cyclanes make up 21-45%. The content of aromatic hydrocarbons is limited to 20-25 wt.%. Besides these, trace amounts of olefin hydrocarbons are observed in fuels; among these, evidently, first place is occupied by alkylaromatic hydrocarbons with unsaturated bonds in the side chain.

The second group includes impurities of heteroorganic compounds (oxygen, sulfurous, nitrous) and also mineral contaminations and moisture. Until recently their presence in fuels was not given its proper value; it was considered that in connection with their small content, their negative influence on fuel was insignificant. With the growing complexity of fuel supply systems of aircraft, whose operation is characterized by ever greater speed, load capacity, and range, the negative role of nonhydrocarbon impurities in the operational properties of jet fuels became essential. The development of a number of measures for combatting the negative influence of nonhydrocarbon compounds on fuel properties was required.

However, the quantity of nonhydrocarbon impurities in fuel is not so very small. The following approximate calculation gives some idea of this. Taking the molecular weight of heteroorganic compounds or equal to the "average" molecular weight of the fuel in which they are present and assuming in a molecule only one hetero-atom, we will obtain (in %):

Sulfur compounds (sulfur to 0.25%)	1.25
Nitrogen compounds (nitrogen to 0.02%)	0.10
Oxygen compounds (oxygen to 0.02%)	0.10
Total	1.45

Besides this, standard fuel usually contains 2-4 g per ton of micrccontaminations in the form of solid phase and 0.003-0.005% dissolved water. Thus the total nonhydrocarbon impurities in contemporary standard jet fuels can approach 1.5%. We will add that in certain conditions the quantity of oxygen compounds, microcontaminations, and water can noticeably increase.

If during heating of the fuel only one percent of the total nonhydrocarbon impurities are turned into solid insoluble sediment, there will be formed 10-15 mg of sediment per 100 ml of fuel. This quantity of sediment is sufficient so that 1-2 hr of circulation of fuel can dirty the filtering element, bringing the resistance on the filter to an impermissibly great magnitude.

On the whole, the chemical composition of fuels depends on the composition of the crude and the methods of its processing. In fuel obtained from Azerbaidzhan crudes there are more cyclane hydrocarbons, and in fuels from Volga crudes, more alkane and sometimes aromatic hydrocarbons.

Hydrocarbons

The effort to increase the heat of combustion per unit weight of contemporary jet fuels has led to the necessity of deep study of the chemical structure of the hydrocarbon components of the fuel. We studied hydrocarbon mixtures distilled within the limits 100-350°C obtained from various crude oils in industrial conditions of processing. Fractions of hydrocarbon mixtures were separated from diesel fuels and fuels of type "T" obtained from Azerbaidzhan, Volga, Groznyy, and Far Eastern crudes; from products obtained after dearomatization, catalytic cracking, hydrogenation; from the high-boiling part of alkylate, composed completely of alkane hydrocarbons of isomeric structure; from hydrocarbon fractions obtained by hydrogenation of lignite; and so forth. The hydrocarbon mixtures were separated on the column into 50-degree fractions, which were then subjected to chromatography. Depending upon the nature of the initial mixture, we obtained narrow fractions of alkane, cyclane, alkane-cyclane, and monocyclic hydrocarbons; in all about 100 50-degree fractions, monotypic in chemical structure of different origin. The characteristics

of the hydrocarbon fractions, freed during chromatographing of moisture, and oxygen and tarry compounds are given in Table 21.

Almost all hydrocarbon fractions, independently of origin and structure, which were separated from fuel mixtures and which boiled prior to 200°C had very low pour points — below minus 68°C (Table 21). For the monocyclic aromatic hydrocarbons this property was retained in fractions boiling prior to 350°C. As regards the majority of cyclane, alkane, and alkane-cyclane hydrocarbons evaporating within the limits 200-350°C, for them (with the exception of a few) the freezing point or pour point was increased. This depended on the branching of alkane hydrocarbons and the structure of the lateral aliphatic chains at the cyclane ring.

Table 22 contains limiting values of the characteristics of fractions and the chemical structure of the constituent hydrocarbons. In none of the fractions were cyclical hydrocarbons without lateral side chains found.

For monocyclic cyclane hydrocarbons, with an increase in the boiling point from 100 to 350°C the number of carbon atoms in the side chains grew from 3 to [illegible]; for aromatics it grew from 2 to 12. Consequently the cyclane and monocyclic aromatic hydrocarbons of every fraction are close in terms of branching of side chains.

The change in the specific heats of combustion per unit weight in [illegible] for optimum structure the increase occurs within the limits [illegible] kcal/kg. Practical utilization of this possibility is made extremely difficult by the complexity of obtaining fuels of such directional composition.

The possibilities for increasing the volume heat of combustion are less limited, inasmuch as the density of hydrocarbons varies in quite wide limits, depending upon the quantity and compactness of the arrangement of side hydrocarbon chains. The limits of increase of the volume heat of combustion for hydrocarbons with structures which are optimum from this point of view can be estimated as 300-700 kcal/liter, i.e., 3-4 times more than for specific heat of combustion per unit weight. In this respect the advantage lies with the cyclane and monocyclic aromatic hydrocarbons. This circumstance forces us to pay somewhat more attention to the appraisal of the properties of cyclical hydrocarbons. Till now the presence in fuel of aromatic hydrocarbons, independently of their structure, was limited. It is known that aromatic hydrocarbons lower the burning properties of fuel; they are characterized also by somewhat heightened hygroscopicity. Monocyclic aromatic hydrocarbons of fuel fractions of industrial production are characterized by the presence of a large number

of carbon atoms in the side aliphatic chains, which improves their burning properties and increases their specific heat of combustion per unit weight. Hydrocarbons of such structure are very stable and have low freezing points. The properties, reserves, and contemporary methods of industrial extraction of monocyclic aromatic hydrocarbons from hydrocarbon mixtures (methods of chromatography, selective extraction, etc.) indicate a need to allot more attention to the use of monocyclic aromatic hydrocarbons in the composition of jet fuel than has been done up till now. Cyclane hydrocarbons with short side chains also possess good properties.

Table 21. Characteristics of Fifty-Degree Hydrocarbon Fractions of Fuels of Different Origins

Refractive index n_D^{20}	Density ρ_4^{20}	Freezing point or pour point, °C	Molecular weight	Elemental composition, %		Average formula	Empirical formula	Lowest heat of combustion, kcal, per		Note
				C	H			1 kg	1 liter	
I. Boiling point 100-150°C										
1. Alkane hydrocarbons										
1.4176	0.7412	Below — 68	114.4	84.40	15.60	$C_{7,8}H_{17,4}$	$C_nH_{2n+1,8}$	10 490	7911	
2. Cyclane hydrocarbons										
1.4510	0.8207	"	139.1	85.63	14.32	$C_{9,9}H_{19,9}$	$C_nH_{2n+0,1}$	10 255	8416	
3. Alkane-cyclane hydrocarbons										
1.4111	0.7312	"	111.5	85.22	14.90	$C_{7,9}H_{16,8}$	$C_nH_{2n+0,8}$	10 476	7657	Cyclanes — 22.4% Alkanes — 77.6%
1.4114	0.7362	"	121.3	84.72	15.37	$C_{8,6}H_{16,5}$	$C_nH_{2n+1,8}$	10 540	7760	Cyclanes — 41.4% Alkanes — 58.6%
1.4221	0.7634	"	125.2	85.15	14.83	$C_{8,9}H_{16,4}$	$C_nH_{2n+0,8}$	10 418	7953	Cyclanes — 68.1% Alkanes — 31.9%
1.4349	0.7906	"	131.0	85.47	14.50	C_9H_{18}	C_nH_{2n+1}	10 309	8174	Cyclanes — 90.8% Alkanes — 9.2%
4. Monocyclic aromatic hydrocarbons										
1.4815	0.8589	"	100.4	88.89	10.75	$C_{6,4}H_{11,6}$	$C_nH_{n+0,7}$	9 859	8469	
1.4772	0.8515	"	110.6	89.07	11.03	$C_{8,2}H_{12,2}$	$C_nH_{n+0,8}$	9 902	8217	
1.4838	0.8522	"	117.3	89.0	10.91	$C_{8,7}H_{12,7}$	C_nH_{n+1}	9 945	8475	
II. Boiling point 150-200°C										
1. Alkane hydrocarbons										
1.4298	0.7573	"	164.4	84.72	15.30	$C_{11,6}H_{25,1}$	$C_nH_{2n+1,9}$	10 369	7852	
2. Cyclane hydrocarbons										
1.4510	0.8107	"	139.1	85.63	14.32	$C_{9,9}H_{19,9}$	$C_nH_{2n+0,1}$	10 255	8309	
1.4307	0.7926	"	142	84.84	14.55	$C_{10}H_{20,0}$	$C_nH_{2n+0,0}$	10 419	8259	
1.4348	0.7986	"	143.5	85.51	14.05	$C_{10,2}H_{21,0}$	$C_nH_{2n+0,8}$	10 295	8222	
1.4393	0.7985	"	145.6	85.57	14.41	$C_{10,4}H_{21,0}$	C_nH_{2n}	10 304	8225	
1.4455	0.8143	"	147.2	85.65	14.10	$C_{10,5}H_{20,8}$	$C_nH_{2n+0,2}$	10 295	8379	
1.4406	0.8014	"	148.7	85.70	14.30	$C_{10,7}H_{21,5}$	$C_nH_{2n+0,1}$	10 309	8259	
1.4400	0.7985	"	158.7	85.77	14.23	$C_{11,2}H_{22,6}$	$C_nH_{2n+0,2}$	10 309	8230	
1.4518	0.8230	"	196.4	85.08	14.50	$C_{14,1}H_{28,5}$	$C_nH_{2n+0,3}$	10 304	8362	

Table 21 (Continued)

Refractive index n_D^{20}	Density ρ_4^{20}	Freezing point or pour point, °C	Molecular weight	Elemental composition, %		Average formula	Empirical formula	Lowest heat of combustion, kcal, per		Note
				C	H			1 kg	1 liter	
3. Alkane-cyclane hydrocarbons										
1.4279	0.7982	Below	131.7	85.25	14.70	$C_{9.4}H_{19.4}$	$C_nH_{2n+0.6}$	10 426	7989	Cyclanes -- 60.4% Alkanes -- 39.6%
1.4189	0.7514	Below — 65	131.8	84.65	15.22	$C_{9.3}H_{20.0}$	$C_nH_{2n+1.4}$	10 488	7880	Cyclanes -- 55.8% Alkanes -- 44.2%
1.4371	0.7939	» — 68	144.0	85.58	14.30	$C_{10.3}H_{21.1}$	$C_nH_{2n+0.5}$	10 340	8210	Cyclanes -- 91.0% Alkanes -- 9.0%
1.4366	0.7950	»	149.4	85.40	14.80	$C_{10.6}H_{21.8}$	$C_nH_{2n+0.8}$	10 390	8265	Cyclanes -- 95.8% Alkanes -- 4.2%
4. Monocyclic aromatic hydrocarbons										
1.4781	0.8985	»	128	88.80	11.21	$C_{9.4}H_{14.8}$	$C_nH_{n+4.9}$	9 966	8305	
1.4970	0.8744	»	128.6	89.20	10.75	$C_{9.6}H_{13.9}$	$C_nH_{n+4.3}$	9 890	8648	
1.5023	0.8931	»	128.8	89.13	10.78	$C_{9.6}H_{14}$	$C_nH_{n+4.4}$	9 900	8705	
1.4822	0.8813	»	131.7	88.80	11.32	$C_{9.7}H_{14.9}$	$C_nH_{n+5.2}$	9 950	8470	
1.4982	0.8777	»	134.9	88.70	11.10	$C_{10}H_{15}$	C_nH_{n+5}	9 920	8700	
1.4922	0.8788	»	138.8	88.88	11.07	$C_{11}H_{15.4}$	$C_nH_{n+4.4}$	9 890	8670	
1.4953	0.8780	»	146.5	89.15	11.11	$C_{10.9}H_{13.3}$	C_nH_{n+2}	9 903	8695	
1.5101	0.8988	»	151.1	89.02	10.85	$C_{11.2}H_{13.4}$	$C_nH_{n+5.2}$	9 945	8938	
1.5089	0.8764	»	162.4	89.99	9.90	$C_{12.2}H_{16.1}$	$C_nH_{n+2.9}$	9 078	8482	

III. Boiling point 200-250°C

1. Alkane hydrocarbons

1.4339	0.7762	Below — 68	174.8	84.90	15.10	$C_{12.4}H_{26.5}$	$C_nH_{2n+1.7}$	10 475	8131	

2. Cyclane hydrocarbons

1.4171	0.8112	»	165	85.15	14.30	$C_{11.7}H_{23.6}$	$C_nH_{2n+0.2}$	10 325	8377	
1.4402	0.8164	»	167.5	85.55	14.42	$C_{11.9}H_{24.2}$	$C_nH_{2n+0.4}$	10 446	8527	
1.4550	0.8321	»	168.0	85.14	14.07	$C_{11.9}H_{24.6}$	$C_nH_{2n+0.8}$	10 329	8595	
1.4582	0.8421	Below — 30	169.8	85.00	14.90	$C_{12}H_{25.3}$	$C_nH_{2n+1.3}$	10 313	8685	
1.4528	0.8202	» — 68	170.6	85.26	14.45	$C_{12.2}H_{24.6}$	$C_nH_{2n+0.2}$	10 313	8524	
1.4409	0.8130	» — 20	172.4	85.68	14.58	$C_{12.3}H_{25.1}$	$C_nH_{2n+0.5}$	10 404	8458	
1.4485	0.8178	» — 25	180.2	85.63	14.46	$C_{12.9}H_{26}$	$C_nH_{2n+0.2}$	10 309	8470	
1.4528	0.8266	» — 68	184.5	85.11	14.87	$C_{13.1}H_{27.5}$	$C_nH_{2n+1.3}$	10 345	8552	
1.4543	0.8273	»	224.2	85.48	14.46	$C_{16}H_{32.4}$	$C_nH_{2n+0.4}$	10 333	8540	

3. Alkane-cyclane hydrocarbons

1.4278	0.7611	Below — 27	148	85.10	14.83	$C_{10.5}H_{22}$	C_nH_{2n+1}	10 505	7998	Cyclanes -- 18.5% Alkanes -- 81.5%
1.4382	0.7805	» — 4	156.5	85.30	14.70	$C_{11.1}H_{23}$	$C_nH_{2n+0.8}$	10 384	8109	Cyclanes -- 64.5% Alkanes -- 35.5%
1.4429	0.7903	» — 49	164.4	85.56	14.43	$C_{11.7}H_{23.7}$	$C_nH_{2n+0.3}$	10 355	8245	Cyclanes -- 60.0% Alkanes -- 40.0%
1.4443	0.8014	» — 64	164.4	85.53	14.42	$C_{11.7}H_{23.7}$	$C_nH_{2n+0.3}$	10 392	8328	Cyclanes -- 70.8% Alkanes -- 29.2%

Table 21 (Continued)

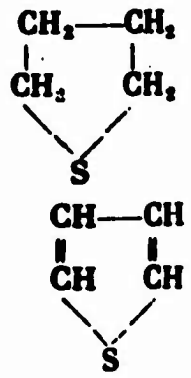
Refractive index n_D^{20}	Density ρ_4^{20}	Freezing point or pour point, °C	Molecular weight	Elemental composition, % C	Elemental composition, % H	Average formula	Empirical formula	Lowest heat of combustion, kcal, per 1 kg	Lowest heat of combustion, kcal, per 1 liter	Note
				4. Monocyclic aromatic hydrocarbons						
1,5000	0,8855	Below — 68	136,2	89,03	10,80	$C_{10,1}H_{14,7}$	$C_nH_{n+4,6}$	9844	8717	
1,4960	0,8773	»	148	88,70	11,42	$C_{10,9}H_{16,9}$	C_nH_{n+6}	9900	8685	
1,4924	0,8949	»	152	88,34	11,28	$C_{12,7}H_{17,0}$	$C_nH_{n+4,3}$	9939	8814	
1,5050	0,8950	»	153,7	89,06	11,19	$C_{11,4}H_{17,2}$	$C_nH_{n+5,8}$	9897	8857	
1,5121	0,9011	»	156,5	89,21	10,46	$C_{11,6}H_{17,2}$	$C_nH_{n+5,6}$	9881	8903	
1,5081	0,9045	»	158,9	88,95	10,33	$C_{14,6}H_{16,4}$	C_nH_{n+2}	9872	8930	
1,5122	0,9024	»	159,2	88,42	10,93	$C_{11,7}H_{17,4}$	$C_nH_{n+5,7}$	9847	8896	
1,5100	0,9066	»	163,9	88,70	10,87	$C_{12,1}H_{17,8}$	$C_nH_{n+5,7}$	9881	8959	
1,5119	0,9173	»	168,9	88,93	10,95	$C_{13,5}H_{18,5}$	C_nH_{n+6}	9911	9001	
1,5072	0,9037	»	172	88,87	11,14	$C_{12,7}H_{19,2}$	$C_nH_{n+6,5}$	9941	8989	
				IV. Boiling point 250-300°C						
				1. Alkane hydrocarbons						
1,4185	0,8037	»	226,2	84,86	15,00	$C_{16}H_{34}$	C_nH_{2n+2}	10 310	8285	
				2. Cyclane hydrocarbons						
1,4585	0,8368	»	183,8	85,76	14,24	$C_{13,1}H_{26,2}$	C_nH_{2n}	10 317	8633	
1,4510	0,8223	Below — 9	196,3	85,28	14,51	$C_{14}H_{28,5}$	$C_nH_{2n+0,5}$	10 308	8476	
1,4558	0,8283	— 12,5	197,3	85,62	14,14	$C_{14}H_{27,9}$	C_nH_{2n}	10 347	8571	
1,4609	0,8366	+ 4	213,5	85,25	14,67	$C_{15,1}H_{31,3}$	$C_nH_{2n+1,1}$	10 155	8699	
1,4602	0,8404	Below — 68	216	85,65	14,28	$C_{15,6}H_{31,3}$	$C_nH_{2n+0,1}$	10 272	8636	
1,4580	0,8413	»	222,6	85,91	14,21	$C_{15,9}H_{31,6}$	C_nH_{2n}	10 305	8670	
1,4618	0,8507	— 22	234,3	85,59	14,30	$C_{16,7}H_{33,5}$	C_nH_{2n}	10 337	8850	
				3. Alkane-cyclane hydrocarbons						
1,4409	0,7858	+4	189,2	85,22	14,72	$C_{13,4}H_{27,9}$	$C_nH_{2n+1,1}$	10 429	8195	Cyclanes -- 14.0% Alkanes -- 86.0%
				4. Monocyclic aromatic hydrocarbons						
1,5319	0,9210	Below — 68	152,3	89,31	10,67	$C_{11,3}H_{16,3}$	$C_nH_{n+5,9}$	9783	9009	
1,4968	0,8761	»	166,3	86,73	11,82	$C_{12}H_{19,6}$	$C_nH_{n+7,6}$	9886	8660	
1,5006	0,9002	»	172,4	88,51	11,28	$C_{12,7}H_{19,5}$	$C_nH_{n+6,8}$	9858	9053	
1,5130	0,9147	»	182	88,08	11,09	$C_{13}H_{20}$	C_nH_{n+7}	9932	9084	
1,5190	0,9302	»	195	88,87	11,30	$C_{14,4}H_{22}$	$C_nH_{n+7,6}$	9900	9209	
1,5172	0,9268	»	202,1	88,87	10,78	$C_{15}H_{21,7}$	$C_nH_{n+6,7}$	9882	9158	
1,5101	0,9306	»	215,3	88,72	11,46	$C_{15,9}H_{24,7}$	$C_nH_{n+8,8}$	9987	9353	
				V. Boiling point 300-350°C						
				1. Cyclane hydrocarbons						
1,4672	0,8545	»	263	85,15	14,68	$C_{18,7}H_{37,2}$	$C_nH_{2n-0,2}$	10 250	8767	
				2. Alkane-cyclane hydrocarbons						
1,4492	0,8978	+113	238,6	85,00	14,85	$C_{16,9}H_{35,7}$	$C_nH_{2n+1,9}$	10 362	8305	Cyclanes -- 22.6% Alkanes -- 77.4%
				3. Monocyclic aromatic hydrocarbons						
1,4966	0,8782	—68	180,2	86,35	11,80	$C_{13}H_{21,3}$	$C_nH_{n+8,3}$	9934	8724	
1,5144	0,9237	—59	239,5	88,66	11,25	$C_{17,7}H_{26,9}$	$C_nH_{n+9,2}$	9947	9173	

Table 22. Limits of Change of Characteristics of Hydrocarbon Fractions of Various Origins

Boiling point of fraction, °C	Characteristics	Hydrocarbons			
		Alkanes	Cyclanes	Alkane-cyclanes	Monocyclic aromatic
100-150	Molecular weight	111.4	139.1	111.5-133	109.4-117.3
	Density ρ_4^{20}	0.7412	0.8207	0.7312-0.7906	0.8315-0.8522
	Number of C atoms in side chains of rings	-	3	-	2.1-2.7
	Lowest heat of combustion, kcal/kg	10,490	10,355	10,339-10,540	9,850-9,945
	kcal/liter	7,911	8,498	7,657-8,174	8,217-8,475
150-200	Molecular weight	164.4	139.1-196.4	131.7-149.4	128-162.4
	Density ρ_4^{20}	0.7573	0.7926-0.8230	0.7514-0.7959	0.8385-0.8988
	Number of C atoms in side chains of rings	-	3.9-8.1	-	3.4-6.2
	Lowest heat of combustion, kcal/kg	10,509	10,330-10,410	10,340-10,488	9,678-9,945
	kcal/liter	7,959	8,250-8,552	7,880-8,265	8,305-8,938
200-250	Molecular weight	174.8	165-224.2	148-164.4	136.2-172
	Density ρ_4^{20}	0.7762	0.8112-0.8421	0.7611-0.8014	0.8773-0.9173
	Number of C atoms in side chains of rings	-	5.7-10.0	-	4.1-8.6
	Lowest heat of combustion, kcal/kg	10,475	10,313-10,446	10,355-10,505	9,844-9,959
	kcal/liter	8,131	8,377-8,685	7,996-8,328	8,614-9,091
250-300	Molecular weight	226.2	183.8-234.3	189.2	152.3-215.3
	Density ρ_4^{20}	0.8037	0.8223-0.8567	0.7858	0.8761-0.9366
	Number of C atoms in side chains of rings	-	7.1-10.7	-	5.3-9.9
	Lowest heat of combustion, kcal/kg	10,310	10,155-10,347	10,429	9,783-9,987
	kcal/liter	8,285	8,476-8,856	8,195	8,660-9,353
300-350	Molecular weight	-	263	238.6	180.2-239.5
	Density ρ_4^{20}	-	0.8545	0.8073	0.8782-0.9237
	Number of C atoms in side chains of rings	-	12.7	-	7-11.7
	Lowest heat of combustion, kcal/kg	-	10,259	10,362	9,934-9,947
	kcal/liter	-	8,767	8,365	8,724-9,173

Sulfur Compounds

Sulfurous compounds of jet fuels have been studied insufficiently. The quantity of sulfur in fuel is limited. In fuels of types TS-1 and T-2, obtained from sulfurous crudes, the total sulfur should not exceed 0.25%, and in fuel T-1, obtained from low-sulfur crudes, it should not exceed 0.1%. The most reactive sulfur compounds are the mercaptans, characterized by the group —SH. Sulfur of these compounds is limited in the GOST's and specifications for fuels to very small amounts — less than 0.005%. For the most part jet fuels contain sulfides ($R - S - R_1$). The presence of a certain quantity of derivatives of thiophanes and thiophenes is possible:



and, probably, a very small quantity of disulfides ($R - S - S - R_1$). The greatest part of the sulfur is included in the so-called undetermined "residual" type.

Table 23 gives the group composition (determined by the Ball method [1]) of jet fuel sulfur compounds, standard in terms of all indices with the exception of the mercaptan sulfur content, which for fuels I, III, and IV exceeds the permissible GOST standards [2].

From Table 23 one can see that in fuels of straight-run distillation a considerable part of the sulfur compounds fall in the share of aliphatic sulfides. Of the sulfur compounds formed in fuels, the least stable (subject to processes of condensation and disintegration) are the mercaptans and disulfides; the stablest are the thiophenes, which are not subject to change with heating to 150-200°C.

Table 23. Group Composition of Sulfur Compounds in Jet Fuels

Sulfur compounds	Fuel			
	I	II	III	IV
Total sulfur content, %	0.123	0.219	0.220	0.178
Composition of sulfur compounds in relative % in conversion to sulfur:				
mercaptans	3.26	18.53	23.63	12.35
aliphatic sulfides	51.10	47.50	25.50	63.00
aromatic sulfides	8.15	None	7.08	8.97
disulfides	2.97	14.80	9.74	14.00
Extracted by mercury, including elemental sulfur	2.38	2.96	0.20	1.68
Residual compounds	32.14	16.21	32.85	None

Along with these conventional presentations there exist facts which force us to consider the sulfur compounds of jet fuels in quite another aspect.

It has been noticed that in the presence of sulfur compounds stable fuel starts to absorb oxygen intensively with small heating. The induction period is reduced and the rate of absorption of oxygen increases with the time of oxidation.

It is interesting that a once-oxidized mixture is oxidized a second time at an even higher rate that in the first time. In other words, sulfur compounds in a fuel medium and the primary products of their oxidation continue to be oxidized, at a rate increasing with time and with an increase in temperature, up to precipitation of a solid phase insoluble in fuel.

In fuel held for a prolonged period in storage an increase is noted in the content of sulfur in the composition of gums absorbed by silica gel.

If one were to continue to store fuel in the same conditions, but first to free it from gums and oxygen compounds on silica gel, it is easy to check the accelerated accumulation of new gums and the sulfur passing from the fuel in their composition.

Finally, it has been established that the gums of the low-sulfur fuel T-1 contain a large quantity of sulfur, little inferior to the amount of sulfur in gums separated from fuel TS-1, which is known to contain 3-4 times more sulfur than fuel T-1. This is also observed in the sediments, which should be considered to be products of the further thermal transformation of gums. Thus, independently of the origins of fuels there is a continuous process of transfer of sulfur to gums and sediments. The rate of this transfer is governed by the initial content and

composition of sulfur compounds in the fuels; the duration of the process is set by temperature conditions, the oxidizing medium, and the catalyzing influence of metals.

Thus under the conditions of the temperature of the environment and especially at raised temperature a considerable portion of the sulfur compounds of fuels are subject to oxidation and oxidizing consolidation. Sulfur compounds are one of the basic sources of formation of gums and then also of solid sediment in fuels.

The inclination of sulfur compounds to oxidation is, evidently, on the same level as or close to unstable hydrocarbons of olefin-aromatic and diene structure. Work is being done on differentiating sulfur compounds of different chemical structure in terms of their inclination to oxidation. This will allow us to detect among the sulfur compounds the group of substances which in certain operational conditions has a less negative influence on the quality of fuel. The process of the oxidizing transformation of sulfur compounds proceeds through stages not only of consolidation of molecules, but also stages of incidental splitting off of fragments of low-molecular sulfur compounds which have a corrosive effect on metals, especially non-ferrous (especially on copper and its alloys). Sediment and gums taken from metallic surfaces working in a medium of fuel always reveal large quantities of ash elements and sulfur, even when the fuel is a low-sulfur one [16, 17, 18].

During the chromatographic separation of medium-distillate fuels sulfur compounds are separated chiefly with the aromatic hydrocarbons. Frequently the aromatic hydrocarbons thus separated can, with complete justification, be called concentrates of sulfur compounds; the content of the latter can attain 20-30% in the fraction of monocyclic aromatic hydrocarbons and 40-50% in the bicyclic fraction.

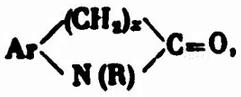
Inasmuch as fuel for supersonic aircraft will be subjected to increased heating, it should be free from sulfur compounds. The complete removal of sulfur compounds from fuel is possible by methods of deep hydrogenation or hydrorefining. Partial removal of sulfur compounds can be done by simpler methods: chromatography, extraction by selective solvents, partial sulfonation, purification over solid absorbents, etc. These measures can be combined with the application of additives which limit the harmful effect of sulfur compounds on the operational properties of fuels.

Nitrogen Compounds

The content of nitrogen compounds in jet fuels is very small. In the residual

products of petroleum processing, 80-90% of the nitrogen compounds are concentrated. Some 1/3 of nitrogen compounds are "basic," inasmuch as they are extracted by solutions of mineral acids, and 2/3 are "neutral." To the "neutral" nitrogen compounds we can add structures which cannot be back-titrated as bases by a solution of chloric acid in an acetate medium. With such a breakdown, the group of "bases" includes homologues of pyridine, quinoline, isoquinoline, acridine, and thiazole, while the group of "neutrals" receives homologues of pyrrole, indole, carbazole, and nitriles and amides of carboxylic acids. Practically no aliphatic and hydrogenated heterocyclic nitrogen compounds are found in petroleum crudes and petroleum products.

N. N. Bezinger, M. A. Abdurakhmanov, and G. D. Gal'pern investigated the chemical structure of "neutral" nitrogen compounds [19, 20]. They came to the conclusion that "neutral" nitrogen compounds of petroleum are chiefly N-substituted amides of carboxylic acids, the most probable structure of which corresponds to the formula



where x = 2 and the hydrogen of methylene groups can be replaced by hydrocarbon radicals.

In other words, "neutral" nitrogen compounds of petroleum represent mainly tertiary aromatic amides, where at least one of the radicals is an aromatic ring with which is directly connected to an atom of nitrogen.

In jet fuels the content of nitrogen is less than 0.1%; however, the presence of nitrogen compounds has an essential influence on the quality of fuels. The compositions of distillates of nonhydrocarbon impurities separated from standard fuels T-1 and TS-1 by chromatographic means on silica gel were found to include the following quantities of nitrogen (Table 24).

Distillates of nonhydrocarbon impurities of the fuels were processed with a 95% aqueous solution of sulfuric acid for separation of nitrogen compounds of a "basic" character. The quantity of nonhydrocarbon impurities extracted thus from the distillate of fuel TS-1 turned out to be insignificantly small; that from fuel T-1 was significant, including 68-71% of the total content of nitrogen. Mixture of the extracted nitrogen compounds contained 6% nitrogen and responded to the empirical formula $C_{12.1}H_{19.1}N_{0.78}S_{0.04}O_{0.33}(C_nH_{n+7})$.

Table 24. Characteristics of Neutral Distillates of Nonhydrocarbon Impurities of Fuels [21]

Indices	Fuels	
	T-1	TS-1
Boiling range of distillates of nonhydrocarbon impurities, °C,		
at 2 mm Hg	27-125	30-118
at normal pressure	170-300	175-190
Density ρ_4^{20}	0.9297	0.9026
Refractive index n_D^{20}	1.4848	1.4775
Molecular weight	168.6	147.6
Iodine number, g iodine/100 g	61.6	91.9
Elemental composition, %:		
C	70.12	75.92
H	11.28	11.87
S	2.08	7.10
N	0.69	0.32
O (by difference)	6.83	4.79
Empirical formula	$C_{11.1}H_{19}S_{0.1}N_{0.08}O_{0.7}$	$C_{9.3}H_{17.5}S_{0.3}N_{0.03}O_{0.4}$
Homologous series	C_nH_{n+8}	C_nH_{n+8}

Study of the narrow fractions of "basic" nitrogen compounds showed that they are characterized by heterocyclic structure, representing mainly derivatives of pyridine.

Nitrogen compounds of fuels are very thermally stable. They are detected in increasing quantities in gums precipitating from the fuels, sediments, and even in scale deposited on the walls of the combustion chamber and injectors, where high temperatures lead to burning out of the less thermally stable sulfur compounds. Along this path nitrogen compounds are subjected to processes of consolidation (condensation and polymerization) and to a smaller degree to oxidation.

The fact that nitrogen compounds are detected in comparatively large quantities in the solid phase, precipitating from the fuel under the influence of heightened temperatures, attests to the fact that they (along with sulfur compounds) are a material participating in the formation of gums, sediment, and scale and therefore are undesirable in the composition of fuels. Substances possessing antioxidant properties are detected in the composition of nitrogen compounds of jet fuels [25].

Oxygen Compounds

Of the nonhydrocarbon impurities in fuels, oxygen compounds can occupy first place in terms of quantity. In distinction from sulfur and nitrogen, compounds,

whose content is determined only by the composition of the oil crude and the method of its processing, the quantity of oxygen compounds can systematically increase. The increase in oxygen compounds is made possible by the oxidation of unstable hydrocarbons of the fuel and by the oxidation of sulfur, nitrogen, and primary [lower] oxygen compounds on the way to the formation of gums and sediment.

Almost all processes of the formation and accumulation of gums and their further thermal transformation are accompanied by an increase of the oxygen in the final substance. The inclination to and rate of absorption of oxygen are used to judge the quality of fuel in one or another condition of operation. Many undesirable processes in fuel could be limited or prevented altogether if it were possible to isolate the fuel from contact with atmospheric oxygen.

Oxidation of an organic substance develops by laws of chain reactions with transformation by stages to the final product of oxidation characteristic for the given conditions. These processes are completed by consolidation, with formation of large molecules. Along with consolidation there will be formed a small quantity of fragmentation low-molecular compounds. Besides radical-chain oxidizing transformations on the way, reactions of an ionic character and also condensation and polymerization can be developed.

What role oxygen plays in processes of transformation occurring in fuels can be judged according to the data in Table 25. With formation of a solid phase, precipitating from the fuel during heating, the share of oxygen in its composition sharply increases.

This gives us a serious basis to consider gums and sediment to be products obtained primarily as a result of oxidizing-consolidating transformations.

By means of chromatographic separation and purification with the application of selective desorbents we were able to separate from jet fuels oxygen compounds satisfactorily purified of other nonhydrocarbon impurities. The characteristics of such compounds, representing the part of the distillate obtained by distillation of nonhydrocarbon impurities separated from fuel, are presented in Table 26.

The oxygen compounds characterized in this table should be considered as intermediate forms on the way to the formation of high-boiling gums, whose further consolidation leads to the formation of a solid phase.

The separated and divided oxygen compound consisted of 30-50% hydroxyl-containing structures, predominantly unsaturated aromatic alcohols, 7-15% complicated ethers, and 30-35% simple ethers.

Table 25. Content of Oxygen in Organic Nonhydrocarbon Impurities and Sediment of Standard Jet Fuels [22]

Fuels	Oxygen, wt.%	Sum of ash elements, wt.%
Nonhydrocarbon impurities separated on silica gel from fuel:		
T-1	10.4	–
TS-1	6.12	–
TS-1	4.10	–
TS-1	4.55	–
T-2	7.93	–
Sediment obtained at 150°C in fuel in contact with bronze:		
T-1	46.56	7.28
TS-1	49.68	7.05

Table 26. General Characteristics of Oxygen Compounds Separated from Distillates of Nonhydrocarbon Impurities [Admixtures?] to Fuels

Indices	T-1		TS-1
	Isopentane fraction	Methanol fraction	Methanol fraction
Density ρ_4^{20}	0.9117	0.9723	0.9345
Refractive index n_D^{20}	1.4774	1.4959	1.4828
Molecular weight	207.9	168.9	157.1
Iodine number, g iodine/100 g	23.7	86.2	73.7
Elemental composition, %:			
C	82.77	78.57	78.01
H	9.64	10.70	10.07
S	0.27	0.21	1.70
N	0.12	0.15	Traces
O (by difference)	7.20	10.35	10.22
Empirical formula	$C_{14.4}H_{20}S_{0.02}N_{0.02}O_{0.94}$	$C_{11}H_{18}S_{0.01}N_{0.02}O_{1.1}$	$C_{10.2}H_{15.8}S_{0.08}O_{1.0}$
Homologous series	$C_nH_{n+5.7}$	C_nH_{n+7}	$C_nH_{n+5.6}$

A small amount of oxygen compounds was characterized by carbonyl and carboxyl groups. Thus all types of compounds characteristic for radical-chain reactions of oxidation of hydrocarbons are detected.

If the process of transformation stopped at this point, such compounds would not render a noticeable negative effect on the operational properties of fuels. However, under the influence of time, an oxygen-containing medium, the catalytic effect of metals, and raised temperature the processes of transformation are completed at a much deeper stage with the formation of complicated nonevaporating structures, comprising gums and then sediment. It is with the formation of the latter that lowered operational qualities of fuels are connected: poor thermal stability, high corrosivity, impaired burning, and other properties.

Mineral Compounds

The content of ashes in jet fuels is limited to 0.003 wt.%. Sources of "ash" compounds, penetrating into the fuel, are in the first place soil dust, and then products of corrosion of storage tanks and pipelines and wear of pumping units. With an increase in temperature the rate of corrosive processes increases. The fuel is "enriched" not only by corrosion products but also by the wear of working mechanisms. Table 27 gives the composition of ash of absolutely dry contaminations held on the 40-micron fuel filters of refueling units and transport aircraft [23].

Table 27. Composition of "Ash" Part of Contaminations of Fuel TS-1 Caught on 40-Micron Filters, %

Composition of ash	Fueling unit	Fuel system of transport aircraft			
	March	November	December	February	April
Iron	30	3—10	3—10	3—10	10
Copper	1,0	11,0	16,0	7,9	13,0
Tin	0,3—1,0	10,0	10,0	10—15	10—15
Cadmium	1,0—3,0	5—10	10,0	10—20	10
Zinc	20—30	1—3	1—3	1—3	1—3
Silicon	3—6	4,0	1—4	1—3	3—10
Aluminum	0,3	3,0	1,0	1,0	1,0
Sodium	0,4—1,0	3—10	3—10	10,0	11,0
Calcium	0,3	3—10	1—3	1,0	1,0
Magnesium	0,1—0,3	1—3	1—3	1—4	1,2
Chromium	—	1,0	0,4—1,0	0,3—1,0	1,0
Nickel	—	0,3—1,0	0,4—1,0	0,4	0,4—1,0
Lead	0,4—1,0	1,0	1,0	0,4—1,0	0,4—1,0
Total ash	70,24	70,34	80,42	73,30	77,92

As can be seen, the ash of contaminants of fuel TS-1 attained 70-90%. Among the mineral impurities there is revealed a large quantity of elements whose sources can be soil dust and the metals of reservoirs, pipelines, and the fuel system of the aircraft, damaged to various degrees in connection with corrosion and with the wear of rubbing parts.

Table 28. Ash of Microcontaminations of Standard Propellants, %

Place of sampling of fuel	Fuel	
	T-1	TS-1
From tank of aircraft:		
I	72.10	—
II	73.54	—
III	63.73	—
From railroad tank car:		
I	78.00	54.53
II	66.15	63.43
III	—	57.2—71.10

In contaminations accumulating in fuels at low temperatures the share of "ash" elements is considerable (Table 28). With an increase in temperature corrosion and wear processes are sharply intensified. Together with this the process of formation of sediments and deposits is intensified. However, the relative content in their composition of ash elements decreases somewhat. The share of the organic part increases.

On the Chemical Composition of Jet Fuels for Supersonic Aircraft

To guarantee the greatest possible range, speed, and height of flight fuel should be distinguished by a large energy content.

Inasmuch as the fuel tanks of supersonic aircraft will be limited in capacity, besides the heat of combustion per unit weight it is important that the fuel be characterized by the greatest possible heat of combustion by volume. The chemical composition of fuel should be such that the burning of the fuel proceeds satisfactorily at great altitudes in conditions of great speed. The fuel should be stable and free from nonhydrocarbon impurities, which will make it possible to exclude the formation of sediment, fouling the filtering elements of fuel system of the engine, with heating of the fuel in flight. Finally, the fuel should be distinguished by good low-temperature properties: the necessary level of viscosity in the entire temperature range of operation, low freezing point (no higher than -45°), low

hygroscopicity, etc. Fuel should have limits of evaporation at which the pressure of its vapor at altitude is sufficiently low and losses from evaporation are insignificant.

These requirements would be satisfied best by a fuel consisting of hydrocarbons of cyclane structure. Cyclane hydrocarbons are characterized by sufficiently high density and both weight and volume heats of combustion, which profitably distinguish it from the alkane hydrocarbons, which have low volume heat of combustion, and aromatics, which have low heat of combustion per unit weight. Cyclane hydrocarbons are sufficiently stable and possess satisfactory burning and low-temperature properties. Alkane hydrocarbons have higher heat of combustion, better burning properties, and 20% greater heat capacity than cyclane hydrocarbons of high density. The latter feature gives considerable advantage to alkane fuels, considering the need for absorption of the heat appearing during supersonic flight.

Some idea about new fuels for supersonic aviation and about the individual hydrocarbons which can be used as components of such fuels is given by the information in Table 29 [24].

As can be seen, hydrocarbons of combined structure, at whose basis there lies the cyclane ring, are characterized by high volume heat of combustion; consequently, by high density, low freezing point, and high boiling point. As regards the heat of combustion per unit weight, there is no significant distinction among the hydrocarbons of their mixtures.

It is doubtful that individual hydrocarbons will be used as the basis of future jet fuels. Such fuels will constitute mixtures of alkane hydrocarbons of isomeric structure and cyclane hydrocarbons with side saturated aliphatic chains in different ratios. However, they will have to be free of nonhydrocarbon impurities. Such fuels may possibly contain polyfunctional additives to secure corrosion passivity, high antiwear properties, prevention of oxidation of hydrocarbons during heating, and so forth. In conditions of transportation, storage, and pumping of these fuels, measures will have to be provided to ensure preservation of their high degree of purity.

Such are some of the prerequisites for the creation of new hydrocarbon jet fuels intended for supersonic aircraft.

Table 29. Characteristics of Certain Fuels, Components, and Hydrocarbons for Fuels of Supersonic Jet Aircraft

Designation	Temperature, °C		Lowest heat of combustion	
	Boiling	Freezing	kcal/kg	kcal/liter
Fuel JP-6 (Mil-F-25656)	Beginning 149	-54	10200	7920
Fuel JP-150 (paraffinic)	Beginning 76.7	-60	10550	7400
Kerosene of high density	Beginning 211	-78	10250	8880
Decahydronaphthalene	182	-69	10150	9150
bis-(methylcyclohexyl)-ethane	288	-40	10240	9280
Isopropylbicyclohexane	274.5	-34	10220	9100
Dimethyldecalin	223	-52.2	10030	10120
Diethylcyclohexane	160	-59.5	10320	8250
Pinane	157	-59.5	10320	8900
Nonane	150.5	-52.3	10570	7610
Cetane	287	+18.13	10470	8150
5,5-dimethyl-4,6-methanespiro(2,5) octane (DMO)	160	-69	10250	9200

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CHAPTER IV

CHANGE IN QUALITY OF JET FUELS DURING STORAGE

A system of checking the quality of fuel by various methods permits judging its fitness for application. Commercial jet fuels, representing chiefly products of straight run distillation of petroleum, consist almost entirely of saturated hydrocarbons, which are very stable. The duration of their storage without noticeable changes in quality should be measured in years. Meanwhile degree of preservation by jet fuels of their operational properties in periods of prolonged storage is a subject of constant discussion. As was shown above, in the United States it is considered useful to introduce antioxidant additives into jet fuels.

Let us consider the changes in quality which are possible in commercial jet fuels in conditions of prolonged storage.

In standard jet fuels, devoid of mechanical impurities visible to the naked eye, with magnification under the microscope it is possible to detect numerous solid particles – microcontaminations. If one were to pass such fuel through biological cellulose acetate film with 0.9 μ pores [1], the weight added to it by the microcontaminations will constitute, after conversion, 0.5-3.5 g per ton of fuel. The less the dimensions of the particles the greater their quantity. In one milliliter of fuel the number of particles with dimensions of 1-5 μ can be a thousand.

Table 30 gives the characteristics of the screen composition of microcontaminations of standard fuels. One might think that the presence of these particles in fuel is connected only with the dustiness of the external medium with which the fuel is in contact. However, the following facts attest that this explanation is not definitive.

Table 30. Microcontaminations of Standard Fuels (Screen Composition)

Place of sampling	Quantity of microcontaminations, g/ton	Quantity of microcontaminations (particles/ml) caught on filters				
		1—3μ	3—5μ	5—10μ	10—20μ	Over 20μ
Fuel TS						
From railroad tank cars	1,10—2,9	4 300—11 200	2 800—4 700	850—3 000	360—1 800	50—250
From sunken tank after settling	1,09—1,11	6 000—16 000	4 400—8 700	150—1 800	370—700	50—200
From surface distribution tank	1,04—1,11	5 000—13 000	2 600—3 500	1 000—1 800	570—800	70--140
Fuel T-1						
From railroad tank cars	1,89—3,23	3 300—7 700	1 200—3 000	400—1 400	100—400	40—120
From sunken tank after settling	1,23—2,67	2 400—2 900	950—1 100	300—500	50—230	30—140
From surface distribution tank	1,50—2,50	≈7 000	≈3 000	≈1 300	≈500	≈200

Both during storage of fuel with access of air and also during hermetic storage the quantity of particles of microcontaminations in the fuel increases.

This was observed in fuel prefiltered with a fineness of filtration of 20-25 μ. The quantity of particles of smallest dimension 1-3 μ, visible only at strong magnification, increased especially strongly (Table 31).

Table 31. Change of Screen Composition of Microcontaminations in Standard Fuel T-1 During Prolonged Storage, particles/ml

Characteristic of dimension of particles	Time of sampling of fuel		
	February	April	July
Open storage, particles with dimension, μ			
1—3	20 750	63 700	104 750
3—5	3 000	3 025	16 450
5—10	1 200	2 000	2 500
10—20	300	370	460
Hermetically sealed storage, particles with dimension, μ			
1—3	23 100	51 000	51 400
3—5	4 700	4 800	9 500
5—10	1 200	1 700	1 900
10—20	300	400	500

The quantity of microcontaminations in the fuel increased with duration of storage and growth of ambient temperature. It turned out that the growth of the quantity of microcontaminations occurred not only because of external contaminations but also because of external contaminations but also because of processes proceeding directly in the fuel.

Let us consider to what limit particles of microcontaminations in fuel can be accumulated.

"Big" particles (dimensions more than 5 μ) in virtue of their weight should in time pass into sediment and settle out. Regarding small particles (less than 5 μ), they will remain in the fuel in suspension for a prolonged period.

Observations have shown that in the fuel there occurs not only accumulation of microcontaminations but also their loss from the fuel in the form of a consolidated phase.

As a result of 4-month storage in the spring-summer period in unheated location of standard fuel TS-1, poured from tanks of aircraft and refueling units, in hermetically sealed 20-liter glass bottles, a considerable increase in the quantity of microcontaminations was revealed. Some of the microcontamination was accumulated directly in fuel and was separated with the help of a supercentrifuge; a much larger quantity of microcontamination was deposited on the walls of the bottles. From the walls of the bottles (after their treatment with isopentane to separate traces of fuel) the microcontaminations were removed with a methanol-benzene mixture. Table 32 shows the content of microcontaminations in the fuel after 4-month storage in hermetically sealed 20-liter glass bottles.

Table 32. Microcontaminations of (Air-Dried) Fuel TS-1 After Storage, g/ton

Number of sample	In fuel	On walls of bottles	Total
1	10.96	7.4	18.36
2	2.37	20.85	23.22
3	0.56	4.18	4.74
4	0.58	2.46	3.04
5	2.08	2.59	4.67
6	0.98	1.27	2.25
7	1.02	3.46	4.48
8	0.80	1.45	2.25
9	0.47	3.38	3.85
10	4.82	10.06	14.85

The amount of microcontamination in the various samples of fuel differed strongly; this depended on the place of sampling of fuel. On the whole the total amount of microcontamination considerably exceeded the quantity detected in standard fuel. In this case the increase in microcontamination occurred because of material contained in the fuel long before the beginning of their formation.

It is obvious that in process of storage a systematic accumulation of microcontamination in fuel proceeds with their simultaneous withdrawal from the fuel in the form of a consolidated solid phase.

It has been established that microcontamination of fuels consists of three

constant components: mineral, organic compounds, and "structural" moisture, i.e., moisture whose weight corresponds to the difference between the weight of air-dry and absolutely dry (dried to constant weight at 105°C) microcontaminations.

The relationship of the mineral and organic parts and moisture can vary. However, in all microcontaminations of fuels, independently of the place of sampling, these constituent elements are constantly found [2]. The constancy of the composition of microcontaminations of fuels and of the consolidated phase precipitating from fuels under the influence of duration of its storage, of contact with atmospheric oxygen and metals, indicated their common source of formation.

Table 33 gives the component composition of microcontamination extracted or precipitating from standard fuels.

Table 33. Composition of Microcontamination of Standard Fuels, % in Air-Dry Matter

Place of sampling and microcontaminations	Content of "structural moisture	Ash
Fuel TS-1		
Tank of aircraft		
after servicing	7.65* / 15.60	63.1 / 39.1
after landing	15.82 / 62.92	55.1 / 37.0
after filter of fine purification	10.34 / 14.42	57.8 / 13.50
Tank of aircraft	21.86 / 13.31	28.8 / 21.2
The same	2.13	71.0
The same, after filter of fine purification	12.3 / 18.6	35.5 / 35.8
Refueling unit	8.51 / 7.57	22.5 / 56.0
The same, after filter	12.75 / 15.3	21.7 / 24.4
Railroad tank car	24.29 / 4.0	19.7 / 49.5
The same	5.8	60.0
	9.4—24.0	52.3—57.4
Fuel T-1		
Tank of aircraft	16.0	62.3
The same	8.5	67.2
"	10.2	57.8
Railroad tank car	6.2	75.0
The same	10.5	61.6

*Numerator shows content of microcontaminations in fuel; denominator, content on bottle walls.

If we take the ash of microcontaminations to be equal in weight to their mineral part, the content of the organic part in microcontaminations is found within the

limits 20-70% of the weight of all microcontaminations, with the exception of one case: as a result of strong sloshing of the fuel in the tank during leading of an aircraft, the precipitating consolidated microcontaminations are strongly irrigated (moisture 63%). The content of moisture in microcontaminations varies strongly (2-63%) and depends on the quantity of water dissolved in the fuel and of water precipitating in the form of the second phase. Consequently water is an active component, taking part in the formation of microcontaminations in fuel.

The ash of microcontaminations of fuels varies in limits just as wide (13-75%). The ash reflects the content in fuel of mineral impurities: products of soil dustiness and of the corrosion of metals and their wear. It is obvious that the mineral impurities in fuel are also active components, taking part in the formation of microcontaminations.

Finally, the third component making up microcontamination of fuels is organic matter. It is interesting that in the products of consolidation of microcontaminations precipitating from fuel in the form of the second phase, the quantity of organic matter in almost all cases considerably exceeds the quantity of inorganic substances in the composition of the microcontaminations remaining in the fuel. Consequently, in the process of consolidation microcontaminations turn out to be highly enriched with organic components participating in the formation of the solid phase along with mineral substances and moisture.

Table 34 gives the elemental composition of absolutely dry microcontaminations of fuel. As can be seen, microcontaminations extracted from fuels, taken from fuel filters, and precipitating on the walls of bottles of fuel contained carbon, hydrogen, sulfur, nitrogen, oxygen, and ash elements.

The quantity of oxygen is great. The oxygen present should be distributed between the organic and mineral components of contaminations. Part of the sulfur, apparently, also will be found in the composition of the mineral components (sulfates). The large quantity of oxygen attests that the formation of microcontaminations, their accumulation in fuel, and their separation in the form of the solid phase are accompanied by processes of oxidation.

The separated organic part of microcontaminations from fuel filters (treatment with chloroform) consisted of the following elements (filters after fuel T-1), %:

	I	II
C	75,30	66,21
H	10,17	11,13
S	1,89	0,95
N	0,81	1,29
O	12,09	20,41

Table 34. Elemental Composition of Microcontaminations of Fuels, % [2, 3]

Place and time of sampling of fuel and microcontaminations	C	H	S	N	Ash element	O
Microcontamination from fuel TS-1						
Railroad tank cars	17,35—27,97	4,38 -10,78	0,15—0,84	0,28 -1,81	25,5 -35,0	26,19 -45,78
Tanks of aircraft:						
in the fuel	—	—	0,75—1,13	0,4—1,67	—	36,39—40,04
on the walls	—	—	0,13—5,47	0,80—2,65	—	32,50—44,90
Storage tanks	12,92	7,52	0,10	0,20	51,24	28,02
Fuel filters of aircraft (40 μ):						
November	21,55	3,48	0,54	0,61	44,07	29,75
December	10,07	1,80	1,70	0,47	56,42	29,54
February	19,16	2,44	0,64	0,64	47,72	29,35
April	12,95	2,02	0,85	0,47	57,02	26,67
Fuel filters of refueling units (March)	8,36	2,43	0,63	0,37	46,18	42,03
Microcontamination from fuel T-1						
Tanks of aircraft.						
I	26,72	6,47	Следы	1,52	29,90	36,39
II	11,61	5,08	0,11	2,47	38,70	42,03
III	20,80	8,60	0,03	1,75	29,23	39,50

Obviously the organic part of the microcontamination constitutes deeply oxidized sulfur, nitrogen, and oxygen organic compounds.

It is necessary to note that microcontamination formed in the low-sulfur fuel T-1 also contain a considerable quantity of sulfur. The composition of the "ash" elements contained in microcontaminations depends on the conditions of storage and the metals in contact with the fuel.

Table 35 gives the composition of the "ash" elements of microcontaminations of certain fuels.

Table 35. Composition of "Ash" Elements of Microcontaminations, %, in Absolutely Dry Substance

Elements	Place of sampling of fuel				
	Railroad tank car	Storage tank	Tanks of aircraft		
			I	II	III
	Fuel TS-1		Fuel T-1		
Iron	6,28—23,67	34	18,89	7,6	4,8
Silicon	4,57—11,50	6,13	7,3	13,1	15,67
Calcium	1,89	2,85	1,98	5,3	3,42
Magnesium	0,97	1,26	1,64	2,64	4,72
Aluminum	0,84	0,82	2,64	3,49	3,97
Copper	0,28	0,02	2,45	0,96	0,02
Zinc	0,20	1,34	1,41	1,65	2,50
Sodium	0,59	0,73	1,77	2,88	2,42
Manganese	—	—	0,08	0,004	0,15
Lead	—	—	0,08	—	—

Among the "ash" elements in microcontaminations there are always considerable quantities of iron and silicon. The fraction of iron in microcontaminations of fuels from railroad tank cars and steel tanks is considerably greater than that in microcontaminations of fuels from aircraft tanks. "Ash" elements formed in aircraft tanks are characterized by larger contents of nonferrous metals in comparison with those formed in tank cars and storage tanks.

On the basis of the presented factual material it is possible to outline the path of the formation of microcontaminations in fuel and their further transformations.

If we take a commercial jet fuel, filter it through a No. 4 glass filter, and examine it under an electron microscope at a magnification of x10,000 we will see no solid particles. Such fuel should be considered to be a homogeneous liquid phase. Six-hour heating of such fuel at a temperature of 150°C in contact with bronze and atmospheric oxygen leads to precipitation of abundant solid phase, easily visible to the naked eye. With small magnification (x80) it is possible to see that this sediment consists of complicated net-like aggregates of various densities and areas. If the fuel with the sediment is filtered again through a No. 4 Schott filter and examined under the electron microscope at the former magnification (x10,000), one will see a large quantity of solid particles less than one micron in dimension.

In this case we are observing a finely-dispersed solid phase in a hydrocarbon medium with particles with dimensions characteristic for a colloidal system (less than one micron, Fig. 20).

The same sequence of transformations can be observed in very stable fuel in which no solid phase is formed during heating, after the introduction of many individual sulfur compounds, not exceeding the permissible GOST [limits].

In this case sulfur compounds are the source of the formation of the solid phase in very stable fuel.

Inasmuch as processes of formation of a solid phase in fuel carry an oxidizing character, it is possible to present the process of transformation of heteroorganic compounds in fuel as follows.

In the initial state sulfur, oxygen, and nitrogen compounds constitute with the hydrocarbon medium of the fuel a homogeneous mixture, corresponding to a true solution. Under the influence of time, temperature, mixing, and contact with metals, atmospheric oxygen develops oxidizing processes at various rates. In these processes

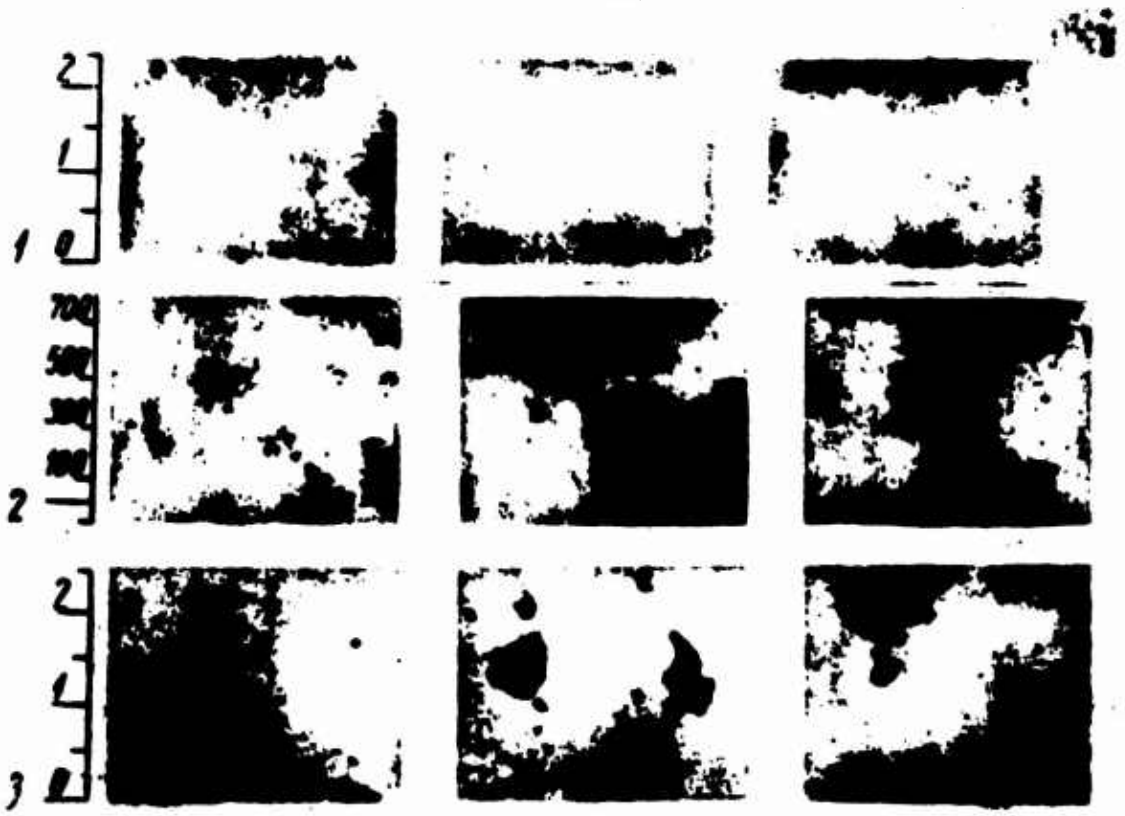

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Fig. 20. Formation in fuel of finely-dispersed phase: 1 — fuel prior tc heating (mag. ×10,000); 2 — fuel after heating at 150° (mag. ×80); 3 — fuel after heating at 150° and filtered through a No. 4 Schott filter (mag. ×10,000).

there are involved, in the first place, the least stable hydrocarbons and sulfur, nitrogen, and oxygen compounds. The majority of primary products of oxidation are still soluble in fuel. But here the formed system is so "overloaded" by heteroatoms that it is in no state to remain further in the fuel in the form of a true solution. Such compounds, approaching in their composition that which is understood by the frequently used term "tarry substances" (gums), are separated from the fuel in the form of a second finely-dispersed phase, at first with particles with dimensions characteristic for a colloidal system (less than one micron); however, the process is not concluded with this. Under the influence of the above-mentioned factors the coagulation of formed particles continues; this leads to the subsequent destruction of the colloidal system with the formation of large particles of the solid phase, precipitating from the fuel. Thus with a rate depending on conditions there occurs, on the one hand, formation of a colloidal system, and on the other, its destruction.

Retarding the oxidation of the entire system as a whole and also the coagulation of the solid phase could limit or prevent precipitation of the solid phase. In the

process of coagulation an accelerating role is played by water and impurities with "ash" elements.

The majority of the products of oxidation of organic compounds are surface-active materials. Water is among the leaders in terms of its surface energy. Changes of the temperature and humidity of the ambient air lead to the presence of water in fuel not only in the dissolved state but also in the form of the finest emulsion, the initial dimension of whose drops is also extremely small prior to the subsequent enlargement and precipitation from the system. The extremely small particles of water sharply activate the process of association of particles of tarry substances and compounds with "ash" elements, forming with them durable aggregates.

The development of this process can be traced (Fig. 21). Figure 21 shows (at ×200) the "collecting" role of water introduced into commercial jet fuels.

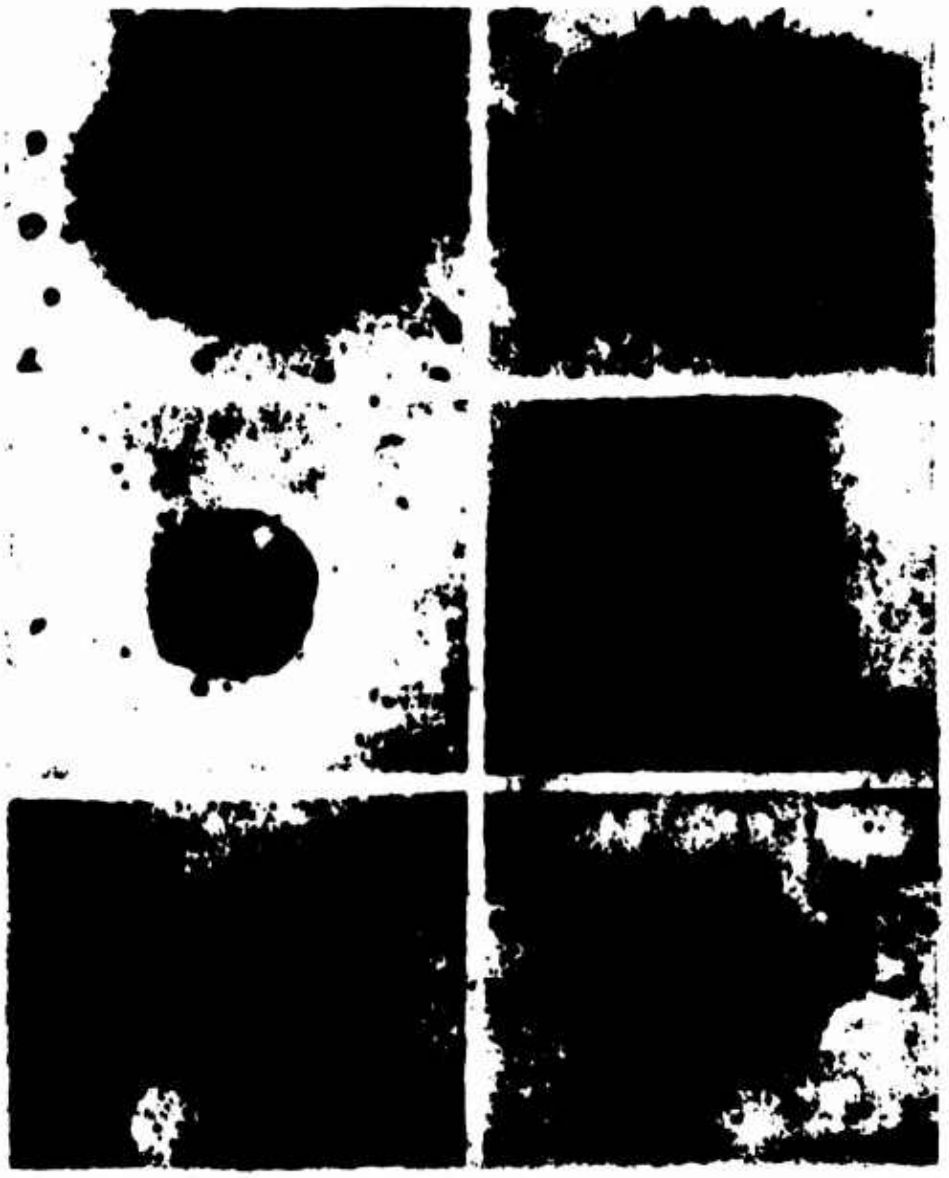

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Fig. 21. "Collecting" role of water among microcontaminations in fuels.

Small particles of impurities with "ash" elements (products of corrosion and wear of metals, soil dust) at a certain stage of the process create, as it were, a framework which is enveloped by tarry substances and water.

This process can be traced in contaminated fuel (Fig. 22).*

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Fig. 22. Coagulation of microcontaminations in two fuels (Mag. ×100).

Let us consider the rate of accumulation of microimpurities in jet fuel.

In fresh, uncontaminated fuel the quantity of microcontaminations is 0.5-1.5 g/ton. After prolonged storage in iron reservoirs, when measures for preventing contamination of the fuel are insufficient, this quantity can reach 3-5 g/ton. In individual cases, when the fuel is subjected to intense mixing in contact with water and precipitating contaminations, the amount of microcontaminations in it can

*Observations and photographs of K. V. Rybakov.

attain the impermissible magnitude of 10-20 g/ton.

The process of accumulation of these microcontaminations proceeds at the temperature of the ambient air. Sediment precipitating from the fuel during its heating has the same origin as microcontaminations accumulated in fuel at the ambient temperature. However, the rate of accumulation of sediment increases intensely during heating. Thus with six-hour heating of fuel in contact with bronze and with access of air at 120°C, in the standard fuel TS-1 there will be formed sediment to the amount of 20-30 g/ton and in fuel T-1, 30-40 g/ton. In the same conditions, but at 150°C, there will be formed in fuel TS-1 80-100 g/ton of sediment and in T-1, 120-150 g/ton.

From this one can see how great is the influence of heating. During multiyear storage of fuel in conditions of the ambient temperature, many times less microcontamination will be formed than during several hours with heating. Other conditions being equal, a difference of 30°C (150-120°C) leads to an increase in sediment by 3-5 times.

Using the above presentations, we can formulate the conditions of the formation and accumulation of microcontaminations in jet fuels during prolonged storage.

In their chemical structure the hydrocarbons constituting commercial jet fuels are stable and can be stored, with observance of certain rules, for many years. However, there exist in such mixtures minute quantities of less stable unsaturated hydrocarbons, which are subject to oxidation even in conditions of storage. Such compounds can make up about 1-1.5 wt.% or 10-15 kg/ton of the fuel. If only a small part of them is subjected to oxidation, for instance aromatic hydrocarbons with unsaturated bonds in the side chains, then this will make up a huge "reserve" for the production of microcontaminations.

Inasmuch as the processes of transformation of unstable hydrocarbons and heteroorganic compounds of fuels carry an oxidizing character, it would seem to be fully reasonable to introduce into such apparently stable fuels small quantities of antioxidant additives, as is accepted in the United States.

For the purpose of limiting the boundary of oxidation of components of fuels by atmospheric oxygen and, together with this, preventing the penetration into the fuel of contaminations from outside, the fuel should be stored in filled, well-sealed reservoirs with effective hydraulic safety valves.

In order to protect the fuel from contamination by products of corrosion, it

is expedient to use an anticorrosion covering on the internal surface of the reservoir.

Stored moisture should, after settling, be systematically drawn off from the reservoir. The addition of fuel should be produced from above, in order not to cause its suspension with moisture and precipitated contaminations concentrated in the lower part of the reservoir. The pumping pipe should be assembled in such a way that it will not open access into fuel of the ambient air and the contaminations contained in it.

Thus, the stability of jet fuel in conditions of prolonged storage is determined not so much by a change of its physicochemical constants as by the content of heteroorganic compounds and the proper conditions of storage, tne prevention of oxidation of unstable components of fuel, accumulation of moisture, and contamination by products of corrosion of metals and surrounding dust.

C H A P T E R V

PUMPABILITY OF JET FUELS

Significance of pumpability. Under pumpability we understand the totality of the physicochemical properties of fuel which determine its ability to be pumped uninterruptedly along the fuel system of an aircraft in accordance with the assigned rule of supply. The quantity of fuel moved into the combustion chamber depends on the operating conditions of the engine and should be constant during an established regime of operation. Disturbance of the supply of fuel leads to impoverishment or enrichment of the fuel mixture, which worsens the conditions of ignition and combustion of fuels and in some separate cases can lead to stopping of the jet engine.

Basic Factors Affecting the Pumpability of Jet Fuels

Fuel feed is influenced by design and operational factors and also by the properties of the fuel itself. At a given construction of the fuel system, the determining influence on process of fuel feed into the combustion chambers of the engines is rendered by the condition of operation of the aircraft and the physicochemical properties of the fuel.

Of the factors pertaining to the conditions of operation, the following have the most essential influence: temperature, pressure, time, humidity of the atmosphere, relative area of contact of the fuel with air, and concentration of oxygen over the surface of the fuel. The most essential effect on pumpability of jet fuels is rendered by the following properties of the fuels: cloud point, temperature of beginning of crystallization, freezing point, viscosity, volatility, density, and inclination to the formation of insoluble gums and sediment with heating.

Pumpability of Jet Fuels at Negative Temperatures

Cooling of Fuel During Storage and Use

During storage and servicing of fuel (in conditions of low temperatures) and also during flights of aircraft the temperature of fuel can be lowered considerably.

Cooling of fuels during storage depends on the temperature of the ambient air. In certain northern regions and also in Central and Eastern Siberia the temperature of the air in winter can attain -60 and even -70°C. During prolonged storage in surface reservoirs at such temperatures fuel will be cooled considerably.

The rate of cooling of fuel depends on the magnitude of the tank in which it is stored. In small reservoirs cooling of fuel occurs rapidly. Thus, during storage of fuel in reservoirs with capacities to 10 tons the temperature of the fuel becomes equal to that of the ambient air as early as in twenty-four hours. With storage of fuel in larger reservoirs the cooling of the fuel occurs more slowly, owing to thermal inertia.

Thus the maximum oscillations of the temperature of fuel, including the deepest cooling, occur during storage in small surface reservoirs and in the tanks of aircraft.

With storage of fuel in large underground reservoirs the oscillations of the temperature of the fuel are insignificant and do not exceed 10°C [6]. In the tanks of aircraft during flight the fuel can be cooled both in winter and in summer, both in northern and sourthern (including tropical) regions. Thus, at heights of 12-30 km the temperature of the ambient air in all regions of the globe attains -60°C [3]. In such conditions at prolonged subsonic speeds of flight considerable cooling of fuel occurs [1, 2, 3].

Cooling of fuel in aircraft occurs quite rapidly. After as little as 2 hr of flight the temperature of the fuel in the tanks of an aircraft is lowered to -25°C and through a certain time attains a minimum magnitude of -30°C. With further flight the temperature of fuel is not lowered [2, 3].

It is possible to consider that at subsonic speeds at altitudes of 12-15 km fuel can be cooled to -30 to -35°C.

During feeding of fuel into the combustion chambers the fuel passes along fuel lines to different aggregates, automatically regulating the quantity of fuel moved, and through filters. At negative temperatures there can be disturbance of normal

fuel feed due to an increase in viscosity and also to precipitation of crystals of ice and certain hydrocarbons (paraffins of normal structure and bicyclic aromatics with 2-3 carbon atoms in the side chains). The increase in viscosity of fuel acts basically as an increase in hydraulic losses in pipelines. The precipitation of crystals of ice and hydrocarbons affects the carrying capacity of filters. The crystals plug the filters, resulting in a sharp decrease in the quantity of fuel moved into the combustion chambers. In connection with this it is expedient to consider the properties of jet fuels affecting the filterability of fuels at negative temperatures and the hydraulic losses in pipelines.

Filterability of Fuels at Low Temperatures

Filterability of fuels depends on the fractional and chemical composition and also on the content of dissolved water.

Filterability of fuels at low temperatures was investigated on an experimental installation [5] simulating the fuel system of an aircraft. The degree of clogging of the filter was determined by the decrease in the flow rate of the fuel. The filter was a metallic grid of square netting with holes of 30-35 μ.

The fundamental diagram of the installation is shown in Fig. 23.

The filterability of fuels T-1, TS-1, T-5, and T-2, which differ in fractional composition, is different (Figs. 24, 25). As can be seen from the given data, with weighting of fuels their filterability worsens. The poorest filterability is shown by fuel T-5 and the best by fuel T-2.

Disturbance of the normal carrying capacity of filter during work on fuel T-5 is revealed as early as a temperature of -20°C. At a temperature of -58°C the feed of T-5 through the filter in 12 minutes is reduced by half.

Disturbance of normal filterability of fuels T-1 and TS-1 occurs at a temperature of -30 to -40°C.

Fuel T-2 is well filtered during cooling to -45°C. Only at a temperature of -50°C, after an hour of work, is there observed a decrease in the carrying capacity of the filter (by 27%) (Fig. 25).

Figures 26 and 27 give data [5] on the filterability of individual hydrocarbon groups separated from fuels T-1 and TS-1 and also show the influence of aromatic hydrocarbons on the filterability of the fuels at various negative temperatures.

Pure fractions of alkane-cyclane hydrocarbons are well filtered at temperatures to -30°C and aromatic, to -20°C.

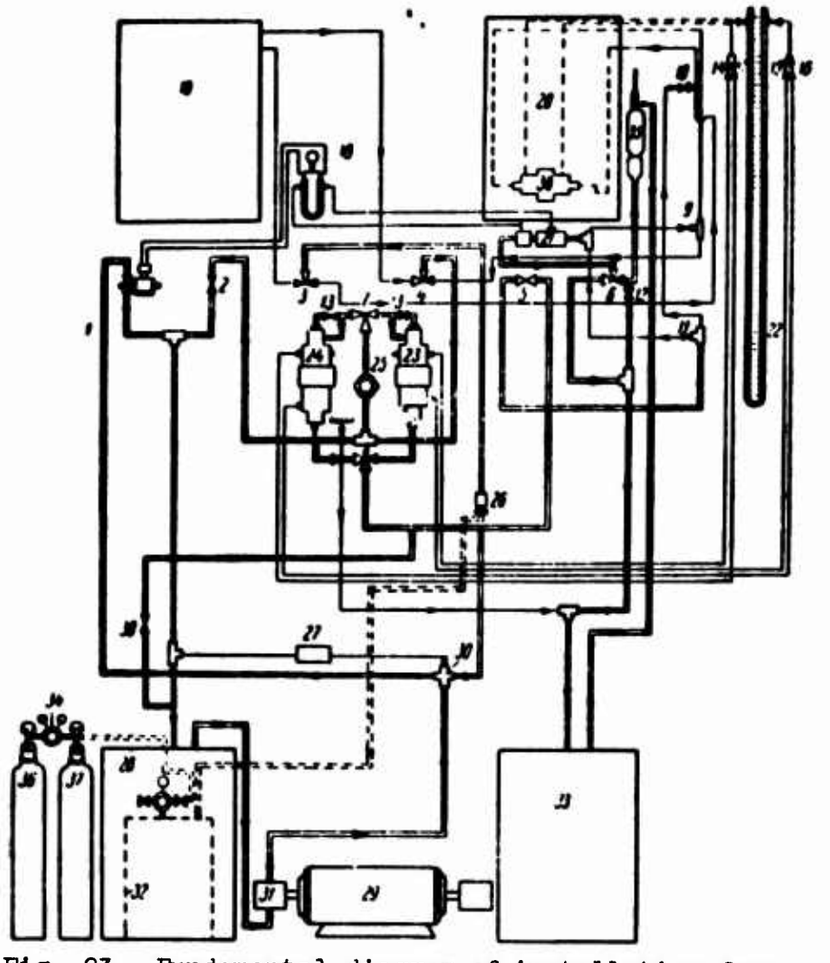

Fig. 23. Fundamental diagram of installation for investigation of pumpability of fuel for air-breathing jet engine. 1 — reduction valve; 2 — adjusting valve; 3, 4, 6-8 — three-way cocks; 5 — choke valve; 9-11 — valves with tees; 12 — cock; 13 — valve: 14-17 — plug cocks; 18, 22 — differential manometers; 19 — heater; 20 — cooler; 21 — flow rate transducer; 23 — right filter; 24 — left filter; 25 — fuel gauge; 26 — filter of coarse purification; 27 — safety valve; 28 — fuel tank; 29 — electric motor; 30 — cross connection; 31 — fuel pump; 32 — autoclave; 33 — dump tank; 34 — reductor; 35 — flowmeter? ["shtikprober"]; 36 — bottle; 37 — receiver; 38 — immersed filter; 39 — valve.

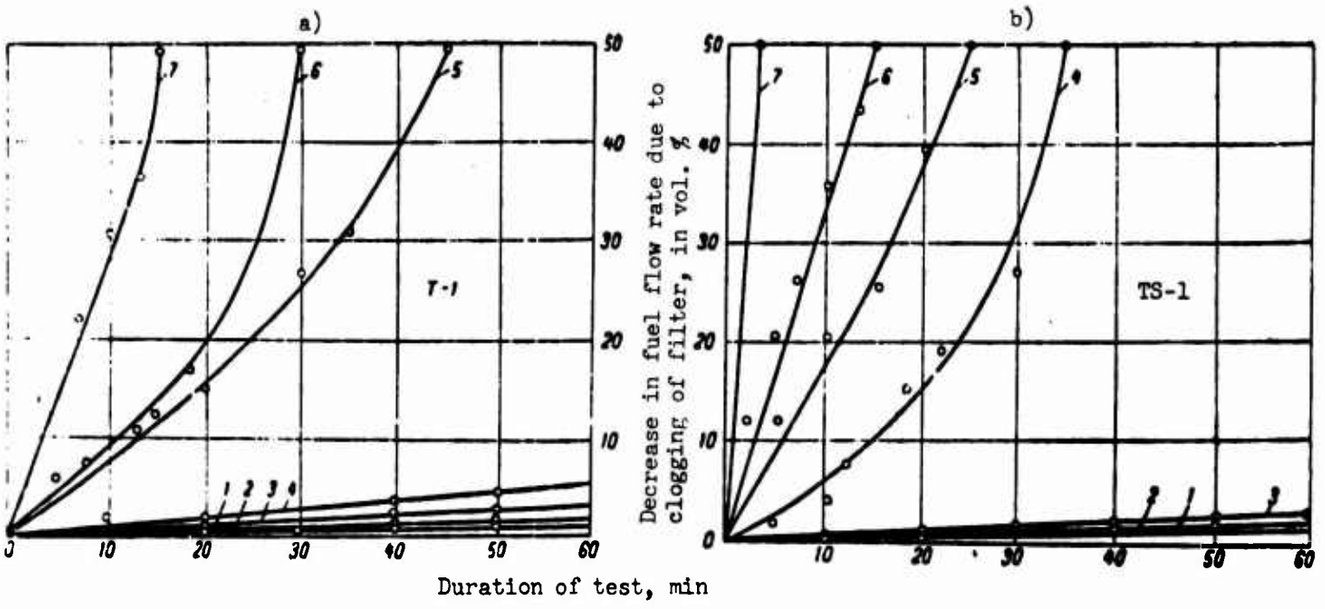

Fig. 24. Influence of temperature on filterability of fuels T-1 and TS-1. 1 – 0°C; 2 – 10°C; 3 – 20°C; 4 – 30°C; 5 – 40°C; 6 – 50°C; 7 – 58°C.

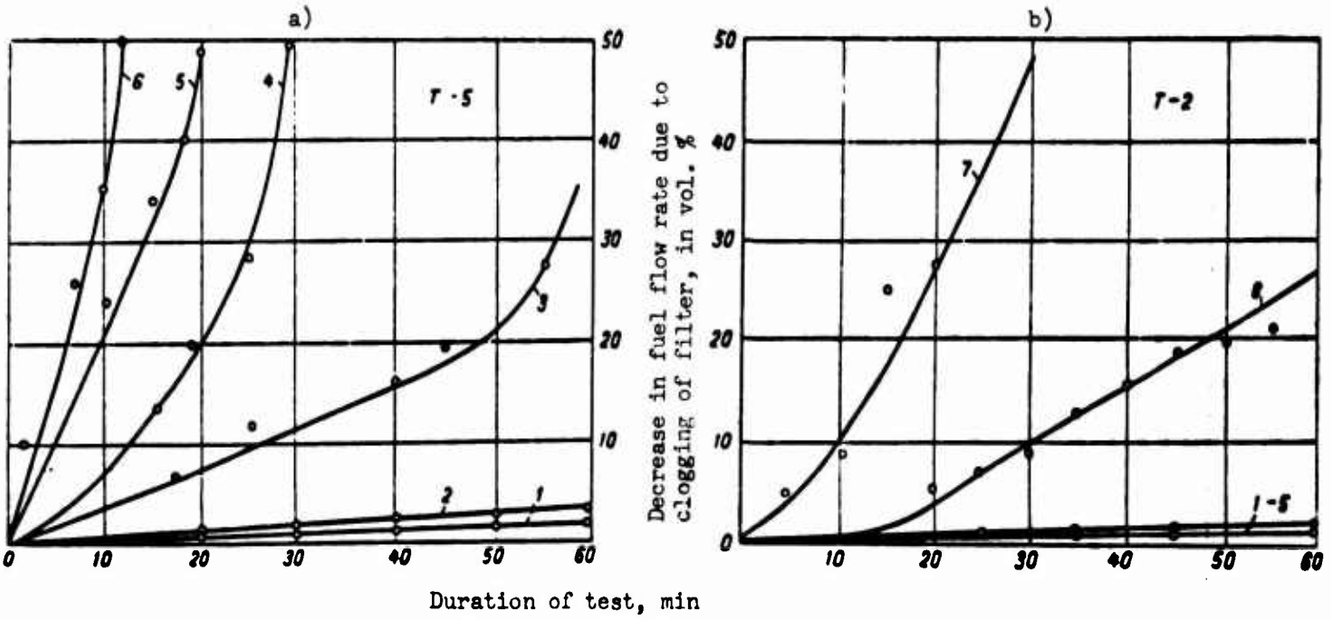

Fig. 25. Influence of temperature on filterability of fuels T-5 and T-2. Designations the same as Fig. 24.

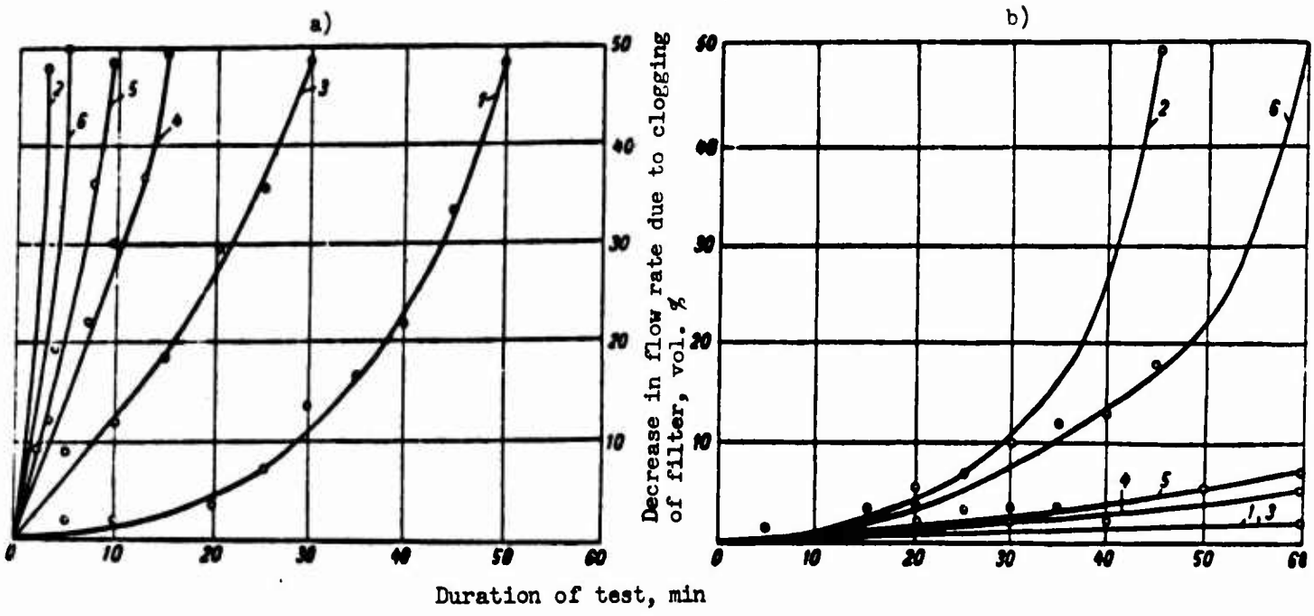

Fig. 26. Filterability of hydrocarbon fractions and artificial mixtures of fuel T-1 at temperatures of -58 (a) and -30°C (b). 1 — alkane-cyclane fraction (ACF); 2 — aromatic fraction; 3 — mixture of ACF with 10% aromatic hydrocarbons; 4 — mixture of ACF with 20% aromatic hydrocarbon; 5 — mixture of ACF with 30% aromatic hydrocarbons; 6 — mixture of ACF with 60% aromatic hydrocarbons.

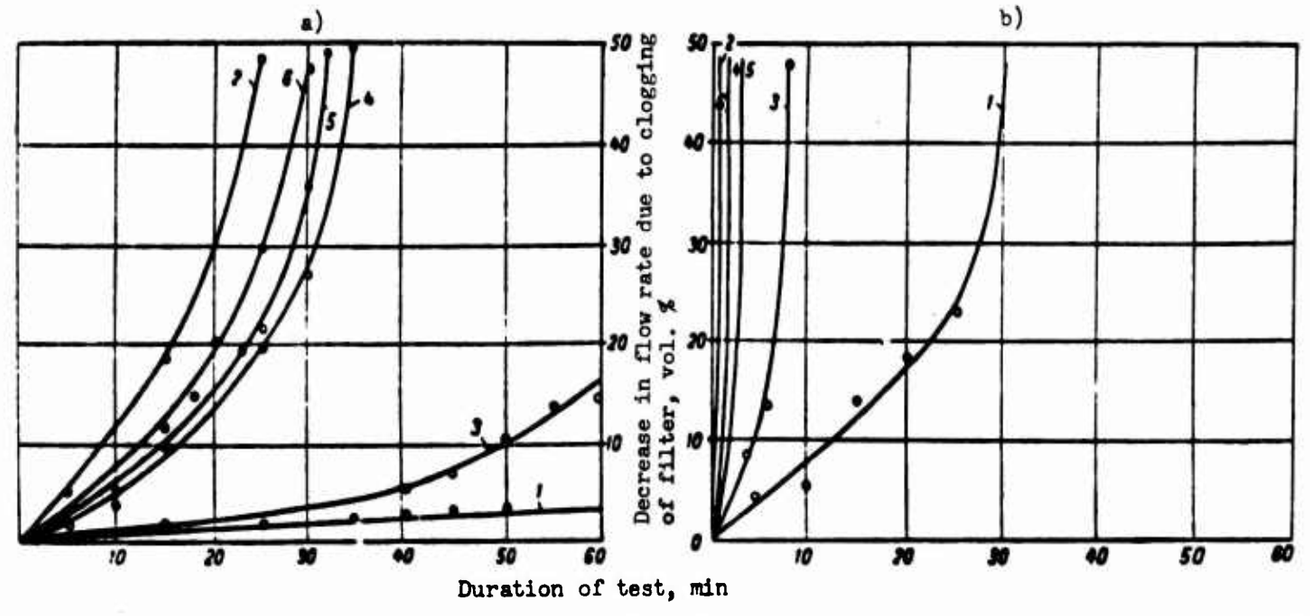

Fig. 27. Filterability of hydrocarbon fractions and artificial mixtures of fuel TS-1 at temperatures of -30 (a) and -58°C (b). Designations the same as Fig. 26.

Table 36. Filterability of Dry and Irrigated Jet Fuels and Their Hydrocarbon Fractions [5]

Fuel and hydrocarbon fractions	Content of water, wt. %	Temperature (in °C) at which the fuel flow rate through the filter decreases by 50%
Fuel T-1:		
dry	Absent	Not decreased to -58
wet	0.008	-40
Aromatic fraction of T-1:		
dry	Absent	Not decreased to -58
wet	0.028	-30
Alkane-cyclane fraction of T-1:		
dry	Absent	—
wet	0.003	-60
Fuel TS-1:		
dry	Absent	Decreased by 18% -58
wet	0.010	-30
Aromatic fraction of TS-1:		
dry	Absent	Not decreased to -58
wet	0.031	-30
Alkane-cyclane fraction of TS-1:		
dry	Absent	-57
wet	0.002	-50
Fuel T-2:		
dry	Absent	Not decreased to -58
wet	0.006	-59
Fuel T-5		
dry	Absent	-52
wet	0.006	-29

With lowering of temperature the filterability of hydrocarbon fractions and their mixtures worsens. The poorest filterability appears in aromatic hydrocarbons, and the best in alkane-cyclanes. With an increase in the content of aromatic hydrocarbon in fuels their filterability worsens (Figs. 26, 27), although aromatic hydrocarbons have the lowest freezing points. The poor filterability of aromatic hydrocarbons is explained by their great hygroscopicity. The latter is confirmed by data in Table 36.

As can be seen from the given data, dehydrated aromatic hydrocarbons filter well to a temperature of -58°C. However, during operation it is impossible to create conditions at which absorption of atmospheric moisture by aromatic hydrocarbons will

be excluded and, therefore, in practice with an increase in the content of aromatic hydrocarbons in jet fuels the filterability of the latter worsens.

Dry TS-1 fuel and the alkane-cyclane fraction separated from this fuel have poorer filterability than the heavier T-1. This should be explained by the large quantity of alkane hydrocarbons contained in fuel TS-1 (see Chapter III).

It is necessary to note that dry jet fuels filter well even with deep cooling; this is connected with the ability of dry fuels to be supercooled up to 70°C. However, in presence even a small quantity of water impairment of filterability of fuels is observed. This is apparently explained by the fact that crystals of ice formed initiate the formation of crystals of hydrocarbons. For instance, in fuel TS-1 containing at +20°C 0.01% water, at -30°C filterability deteriorates by 50% after 35 minutes. At the fuel flow rate in the conditions of the experiment, even if all water was frozen out, 0.25 g of ice would be accumulated on the filter. This quantity of ice is insufficient to lower the transmittance of the filter by 50%. Thus it is fully clear that the precipitation of crystals of ice in the fuel during cooling will initiate formation of crystals of high-melting hydrocarbons (n. alkane and bicyclic aromatics), which will clog the filter.

We can affirm what the limiting content of water determining normal filterability of a fuel should decrease with an increase in the content of high-melting hydrocarbons in the fuel.

It has been noted [5] that the presence in fuel of mechanical impurities, if even their particles are smaller than the holes of filtering elements, have an unfavorable effect on filterability of fuel. Mechanical impurities are, as it were, centers of crystallization not only of hydrocarbons, but also of water.

Generalizing the above, it is possible to affirm that basically the impairment of filterability of fuels is connected with the quantity of water dissolved in them. It follows from this that for essential improvement of the filterability of fuels it is necessary to prevent the escape of water in the form of ice during cooling. Preliminary separation of mechanical impurities and other solid impurities also improves filterability of fuels.

Improvement of Filterability of Fuels at Low Temperatures

The filterability of fuels at low temperatures can be improved by one of the following methods:

– removal from fuels of compounds with high freezing points;

– application of additives which lower the freezing point of fuels;

– application of additives which prevent the precipitation from fuel of water in the form of ice.

The removal from jet fuels of hydrocarbons with high freezing points is not done at present, owing to economic considerations.

Application of additives which lower the freezing points of fuels (pour-point depressants) can be used to improve the filterability of fuels. Several products are known which are applied in as additives to lower the cloud point and freezing point of medium-distillate fuels. These include Paraflow, Santopour, alkylphenols, and the AzNII [Azerbaidjan Scientific Research Petroleum Institute imseni V. V. Kuibyshev] depressant. All these substances consist of asymmetric molecules with high molecular weight. The effect of Paraflow has been investigated in the most detail. Paraflow constitutes a product obtained as the result of condensation of chlorinated paraffin and naphthalene. The effect of Paraflow on the freezing point of fuels is shown in Fig. 28.

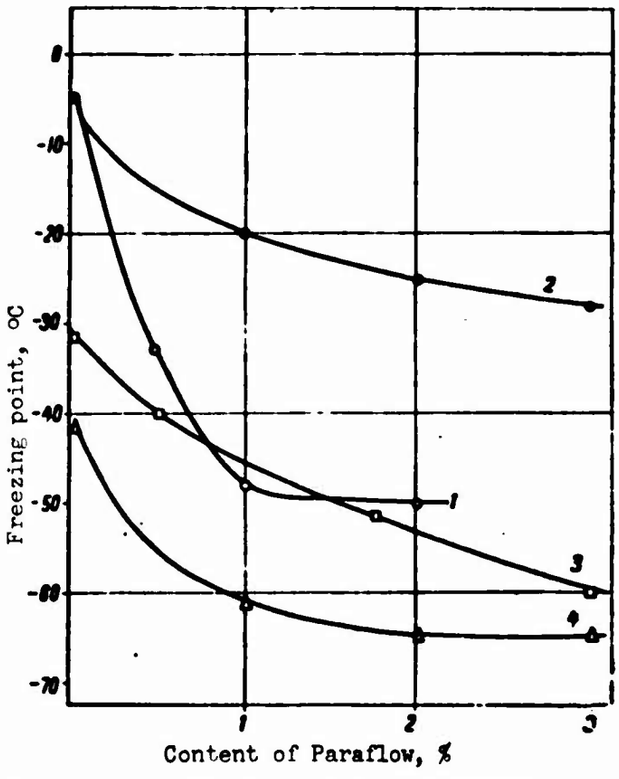

Fig. 28. Influence of the additive Paraflow on the freezing point of fuels [7]. 1 – Surakhan kerosene; 2 – fuel No. 1; 3 – fuel No. 2; 4 – fuel No. 3.

The additive Paraflow effectively lowers the freezing point of fuels [7, 9]. Its effect depends on its concentration and the chemical composition of the fuel. The greatest lowering of the freezing point of fuels is observed with the addition of the first portions of the depressant (up to 1%); with further increase in the concentration of Paraflow the effectiveness of its action is lowered (Fig. 28).

The effectiveness of the action of the depressant depends on the concentration in the fuel of normal alkanes and cyclic hydrocarbons with a long side unbranched chain. The addition of a depressant to fuels with low freezing points does not bring the proper effect. Regarding the mechanism of action of depressants there is no unified opinion [8, 10, 19]. Clearly

Table 37. Speed of Dissolution of Crystals of Ice in Fuel with Addition of Monoethyl Ether of Ethylene Glycol

Quantity of crystals of ice in fuel, wt. %	Temperature of fuel, °C	Amount of additive added to the fuel, wt. %	Time of dissolution of crystals, min
0,01	—40	0,1	60
0,01	—40	0,3	31
0,01	—20	0,1	35
0,01	—20	0,3	17
0,05	—20	0,1	51
0,05	—20	0,3	28
0,05	—5	0,3	3
0,1	—20	0,3	48
0,1	—5	0,3	5

the following opinion should be recognized as the most correct: depressant, being absorbed on the surface of crystals, prevents the further growth of the crystals [8, 18]. At present depressants are not applied for lowering the freezing point fuels; however, some researchers consider that application of depressants will make it possible to improve filterability of jet fuels [20].

The most effective means of improving the filterability of propellants at low temperatures should be recognized as the application of special additives which prevent the precipitation of ice from the fuel during cooling. Ice formation in fuel system of jet aircraft presents a great danger [21, 22] and can be the cause of catastrophe.

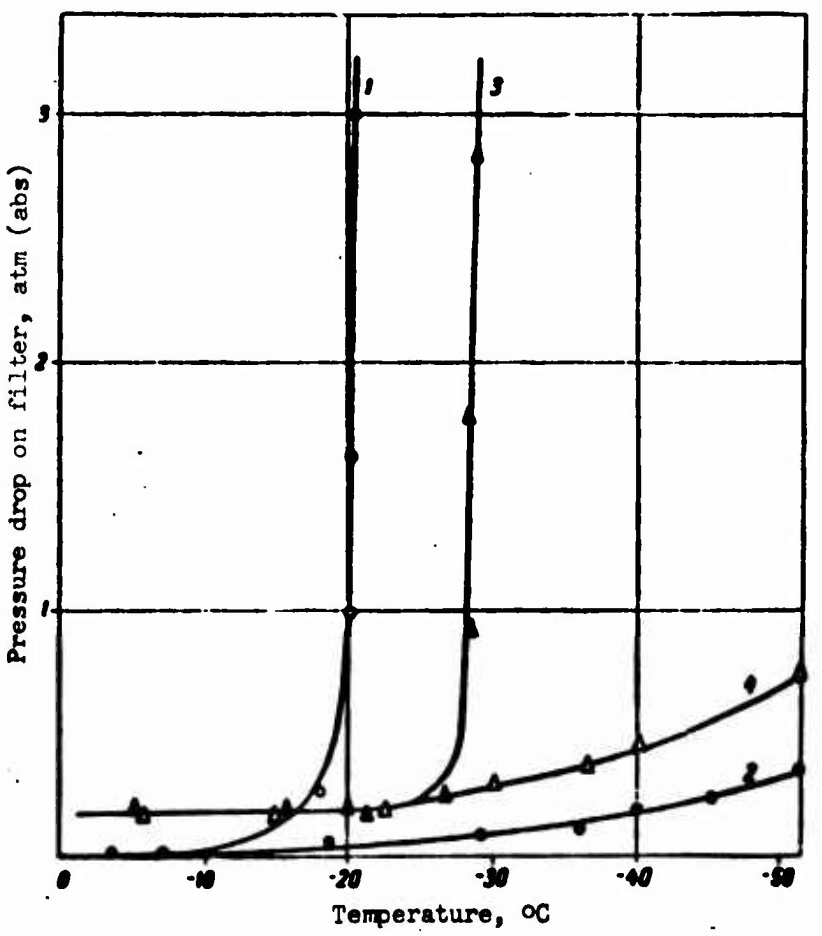

Fig. 29. Influence of monoethyl ether of ethylene glycol on the filterability of propellants at low temperatures. 1 — fuel TS-1; 2 — fuel TS-1 with 0.1% additive; 3 — fuel T-2; 4 — fuel T-2 with 0.1% additive.

To prevent this phenomenon, besides design measures, certain alcohols (isopropyl, ethyl, and methyl) and also certain other liquids are added to fuels. The most effective has been found to be the monoethyl ether of ethylene glycol [5, 18, 23]. This additive well dissolves crystals of ice precipitated from fuel (Table 37) and thereby promotes improvement of filterability of fuels at low temperatures (Fig. 29). As can be seen from the given data, the addition of monoethyl ether of ethylene glycol ensures normal filterability of fuels down to a temperature of

-50°C, while during filtration of these fuels without the additive there is observed a sharp increase of pressure on the filter at temperatures of -20 to -30°C.

Table 38. Influence of Monoethyl Ether of Ethylene Glycol on Filterability of Jet Fuels and Hydrocarbon Groups [5]

Fuel and hydrocarbon groups	Concentration of liquid "I," %	Decrease in flow rate (%) due to clogging of filter at a temperature of				
		-20°C	-30°C	-40°C	-50°C	-58°C
Fuel T-1	Absent	5	12	50.0	Filter is plugged	
Fuel T-1	0.3	None	None	None	None	9.0
Aromatic fraction of T-1	Absent	—	50	—	—	—
Aromatic fraction of T-1	0.3	None	None	None	None	5.5
Fuel TS-1	Absent	—	50	—	—	—
Fuel TS-1	0.3	None	None	None	5.5	48.5
Aromatic fraction of TS-1	0.3	None	None	None	None	5.0
Alkane-cyclane fraction of TS-1	Absent	None	None	7.0	49.0	—
Fuel T-2	Absent	—	—	—	27.0	48.0
Fuel T-2	0.3	None	None	None	5	18.5

With the addition of the monoethyl ether of ethylene glycol there is considerable improvement of filterability of all hydrocarbon groups separated from fuels.

From Table 38 one can see that the monoethyl ether of ethylene glycol improves the filterability of aromatic hydrocarbons, which contain most of the dissolved water. Thus the application of the monoethyl ether of ethylene glycol sharply improves the filterability of wet fuels; the addition of it to dry fuels is meaningless. The monoethyl ether of ethylene glycol does not affect the filterability of fuels if it has deteriorated because of precipitation of crystals of hydrocarbons in dry fuels.

The monoethyl ether of ethylene glycol is usually added to fuels in quantities up to 0.3%. With the introduction of the additive into the fuel the water content is somewhat increased, inasmuch as the additive itself contains 1-2% water. Additives applied for prevention of ice formation in fuels do not have a negative influence on the general operational properties of jet fuels.

Hydraulic Losses in Fuel Lines at Low Temperatures

The pumpability of jet fuels along fuel lines, as was already noted, depends on the viscosity of the fuels. Pumping of highly viscous fuel leads to large hydraulic losses in the fuel system, what leads to a certain decrease of productivity

of fuel pumps and, as a result of this, to lowering of the pressure of injection and impairment of the quality of atomization. During the feeding of excessively viscous fuel, rendering a very large resistance during its flow along the fuel supply system, there may occur breaking of the fuel stream and interruptions in or full cessation of fuel supply. Hydraulic losses in the line can be calculated by the following formula:

$$H_{тр} = \lambda \frac{l}{d} \frac{v_{ср}^2}{2g},$$

[тр = li = line; ср = av = average]

where H_{li} is flow friction of pipeline, m;

λ is drag coefficient;

l and d are the given length and given diameter of the pipeline, m;

v_{av} is the average speed of fuel in the fuel system, m/sec;

g is the acceleration due to gravity, m/sec^2.

During laminar flow

$$\lambda = \frac{64}{Re} = \frac{64\nu}{v_{ср}d},$$

where Re is the Reynolds number;

ν is the kinematic viscosity of fuel, cs.

For every fuel system there exist optimum values of viscosity which ensure uninterrupted operation of the engines. The maximum value of viscosity at which fuel starts to arrive in a quantity which does not ensure rated power of the engine can be conditionally called the limiting viscosity. Since the fuel systems of various aircraft differ from each other in design, the value of limiting viscosity will be different for each fuel system. Complication of the fuel system, as a rule, causes lowering of the value of the limiting viscosity of fuels.

Thus. D. L. Gol'dshteyn, M. V. Veksler and G. Ye. Zhuravlev [4], using an installation which simulated the fuel system of an aircraft, established the limiting viscosity of fuels for three systems as 85, 160, and 210 cs. By proceeding from limiting viscosity of fuel for each fuel system, it is possible to establish the lower limit of permissible temperature of exploitation.

It has been established [5] that there is no essential lowering of the productivity of fuel supply over the fuel system of engines because of an increase in

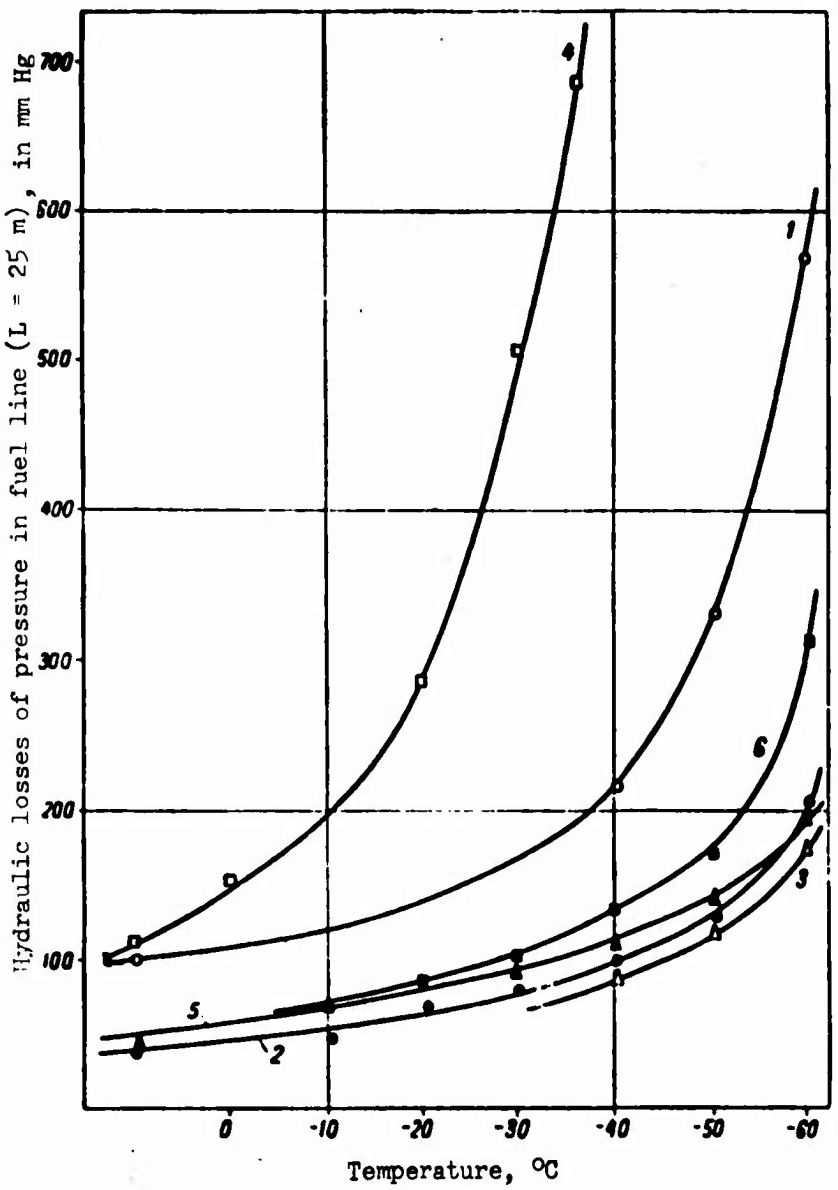

Fig. 30. Hydraulic losses during feeding of jet fuels and hydrocarbon groups over a fuel line at low temperatures [5]. 1 — fuel T-1; 2 — fuel TS-1; 3 — fuel T-2; 4 — fuel T-5; 5 — alkane-cyclane fraction of fuel TS-1; 6 — aromatic fraction of fuel TS-1.

the viscosity of propellants of type T during their cooling to -60°C [5].

It has been shown (Fig. 30) that during the feeding of fuels over a fuel line 25 m in length the most essential hydraulic losses are observed with fuels on the type T-5. During feeding of the other fuels hydraulic losses are relatively small and at a temperature of -60°C do not exceed 600 mm Hg for fuel T-1 and 300 mm Hg for the fuels TS-1 and T-2. Hydraulic losses during circulation of the aromatic fraction of fuel somewhat exceed the losses during circulation of the alkane-cyclane fraction.

Hydraulic losses on a filter with hole diameter of 30-35 μ during circulation of jet fuels at a temperature of -40°C do not exceed 20 mm Hg.

From the above-stated, it follows that hydraulic losses arising in the fuel system on aircraft because of an increase in viscosity are immaterial.

The pumpability of fuels is basically determined by their filterability. Whereas an increase in the viscosity of jet fuels has no material effect on their pumpability over the fuel system, viscosity considerably affects the degree of atomization of fuel by injectors. It is known that for good atomization [5] viscosity of fuels should be no higher than 15 cs. Thus the upper limit of viscosity of jet fuels is limited by just this requirement and not be conditions of pumpability.

Pumpability of Jet Fuels at High Temperatures

Heating of Fuel During Storage and Use

During storage the maximum heating of jet fuels is observed in the summer period in southern regions, where the daytime temperature of the air can attain +70°C. Considering thermal inertia, the temperature of fuel can attain +50°C.

During prolonged storage of jet fuels there are formed insoluble sediment and gum which negatively affect operational properties. These processes develop slowly in the straight-run jet fuels T-1, TS-1, T-2, and T-5 [18]. In conditions of storage, even in hot regions, fuels T-1, T-2, TS-1, and T-5 show no essential change in their properties during storage for 2-3 years.

During application in aircraft with supersonic speeds, possibly a sharp impairment of pumpability of fuels is possible. This is explained by the fact that in contemporary aircraft at supersonic speeds there occurs considerable aerodynamic heating [25-50].

At supersonic speeds there occurs adiabatic compression of air ahead of the aircraft. In this "stagnant flow," owing to compression, the temperature increases sharply. Thus, for instance, at speed of Mach 3 the temperature of the stagnant flow of air at a height of 11 km will be about 330°C, and at Mach 4 it will be about 630°C [45].

The fuel in jet aircraft constitutes 45-55% of the gross weight and at small supersonic speeds (up to 2000 km/hr) is used for cooling the oil, the radar installation, the hydraulic system, the installation for air conditioning, and others. Therefore the fuel is additionally heated. It has been established that at a speed of Mach 2.8 the fuel in the tank (30 t) will be heated after 20 minutes of flight by 70°C; owing to heating in the booster pump and in distributing and regulating devices, the fuel is heated by still another 65-70°C. Taking into account heating in heat exchangers and other aggregates, the temperature of the fuel ahead of the injectors can attain 200°C.

Heating of fuel in the tanks of aircraft can be calculated by the following formula:

$$t_к^т = t_{торм} + (t_н^т - t_{торм})\, e^{-\frac{Fk\tau}{GC_p}},$$

[T = f = fuel; K = fin = final; H = init = initial;
TOPM = st = stagnation]

where t^f_{fin} is the final temperature of fuel, ^oC;

t^f_{init} is the initial temperature of fuel, ^oC;

t_{st} is the stagnation temperature, ^oC;

G is fuel weight, kg;

C_p is the heat capacity per unit weight of fuel, kcal/kg·deg;

k is the heat-transfer coefficient, kcal/m^2·hr·deg;

τ is the time of flight, hr;

F is the surface of tanks, m^2.

The coefficient of heat exchange k is calculated by the formula

$$k=\left(\frac{1}{\alpha_1}+\frac{S}{\lambda}+\frac{1}{\alpha_2}\right)^{-1},$$

where α_1 is the heat-transfer coefficient from air to the fuel tank, kcal/m^2·hr·deg;

S is the thickness of tank walls, m;

λ is the coefficient of thermal conductivity of the material of the tank, kcal/m·hr·deg;

α_2 is the coefficient of heat transfer from the walls of the tank to the fuel, kcal/m^2·hr·deg.

Stagnation temperatures t_{st} can be calculated by the following formula:

$$t_{торм}=t_0\left(1+\frac{M^2}{5}\right).$$

where t_0 is the temperature of flow on external boundary, ^oK;

M is the speed of flight in Mach numbers.

Table 39 gives brief characteristics of modern aircraft and data on the temperature of fuel ahead of the injectors of the engines.

Aerodynamic heating of aircraft at uniform speed of flight increases until an equilibrium is attained between the inflow of heat from friction and its escape into the environment. Aerodynamic heating depends on both speed and altitude. Thus, for instance, at a speed of Mach 4 at 6100 m the equilibrium temperature is established in 90 sec and is 680°C. At the same speed at 36,600 m the equilibrium temperature is established in 30 minutes and equals, in all, 310°C [5].

At temperatures higher than 100°C, existing grades of fuel (T-1, TS-1, T-2 and T-5) are intensely oxidized; as a result insoluble sediments and gums are formed in the fuels, clogging filtering elements of the engines and, being deposited in the

Table 39. Characteristic of Certain Aircraft [25-50]

Type and designation of aircraft	Country	Maximum speed, M	Service ceiling, km	Number of air-breathing jet engines	Calculated limiting temperature of fuel ahead of engine injectors, °C
Fighters					
T-431	USSR	2.5	~20	1	230
E-66	USSR	2.2	~30	1	200
E-166	USSR	3.0	~30	1	250
Lockheed F-104C	USA	2.2	21	1	200
McDonnell F-101B "Voodoo"	USA	2.0	~16	2	190
Northrop N-156F "Freedom Fighter"	USA	2.0	~17	2	120
Republic F-105D "Thunderchief"	USA	2.15	~15	1	210
English Electric P. 1 B "Lightning"	England	2.3	18	2	230
Dassault MD 550 "Mirage III"	France	2.3	22	1	230
Saab I-35B "Dragon"	Sweden	2.0	18	1	190-200
McDonnell F4H-1 "Phantom" II	USA	2.2	21	2	220
"Hawker" P. 1121	England	2.5	23	1	230-240
Bombers					
North American A3U-1 "Vigilante"	USA	2.0	18	2	190-200
Blackburn General Aircraft N.A.39	England	1.5	16	2	120
Convair B-58A "Hustler"	USA	2.0	18	4	190-200
Dassault "Mirage IV"	France	2.0	—	2	190-200
B-70 "Valkyrie" (in development stage)	USA	3.0	20	6	300
Civil transport aircraft					
IL-62	USSR	0.9	13	4	80
TU-104	USSR	0.9	12	2	80
IL-18	USSR	0.8	15	4	70-80
TU-114	USSR	0.9	15	4	80
"Comet-2"	England	0.7	—	—	60-70
"Boeing-707"	USA	0.8	11	4	70

fuel system, disturb the normal operation of the command aggregate, gaps between whose rubbing components compose 8-10 μ [42, 46-49].

Filterability of Fuels at High Temperatures

For investigation of pumpability of jet fuels at high temperatures in the USSR and abroad, special installations which simulate the fuel systems of jet aircraft are used.

In the United States the filterability of fuels is determined on the CFR installation [50], whose fundamental diagram is shown in Fig. 31. The fuel is heated to 150-230°C in an aluminum tube with an electric heater and is passed through a filter with holes of 20 μ. The filter is prepared from fritted power of stainless steel; other filtering elements can also be applied. On the filter the fuel is additionally heated to 205-260°C. The fuel is moved at a constant rate of 2.7 kg/hr at a pressure of 10.5 atm. The test method is standardized [51]. The filterability of the fuels (thermal stability) is estimated by the magnitude of the pressure drop on the filter after 300 minutes of test or, if the filter is clogged earlier, by the test time to achievement of the maximum permissible magnitude of pressure drop (300 mm Hg).

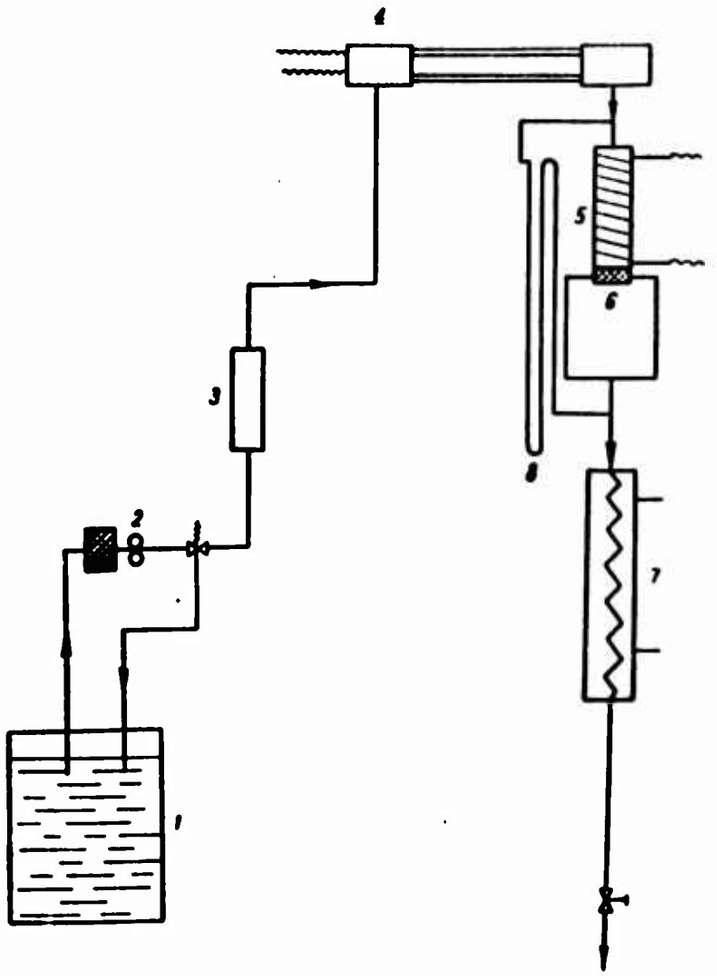

Fig. 31. Fundamental diagram of standard installation CFR for investigation of pumpability of jet fuels at raised temperatures. 1 — fuel tank; 2 — pump; 3 — flowmeter; 4 — heater; 5 — filter holder; 6 — filter; 7 — cooler; 8 — thermometer.

Soviet installations for investigation of fuel filterability differ from the CFR installation in design and in test methods [52-54]. An installation with real fuel aggregates has been created [55].

On [this] installation [53] it

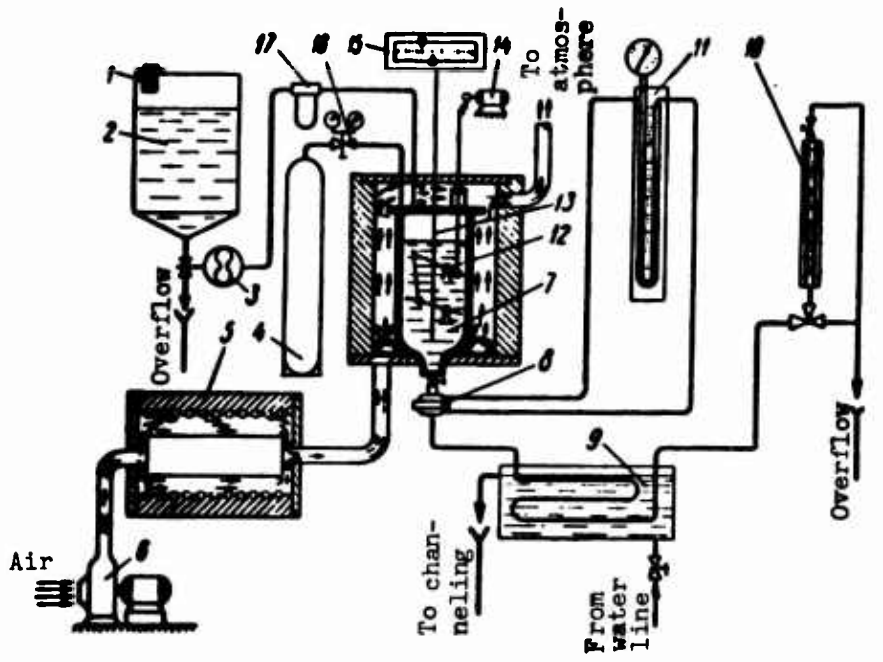

Fig. 32. Diagram of BashNII NP* installation for investigation of jet fuels at high temperatures. 1 – filter of coarse purification; 2 – fuel tank; 3 – pump; 4 – bottle with gas; 5 – heating furnace; 6 – fan; 7 – tank of heat exchanger; 8 – experimental filter; 9 – cooler; 10 – float-type flowmeter [or "shtikhprober" (unidentified - Trans. Ed.)]; 11 – differential manometer; 12 – mixer; 13 – thermocouple; 14 – electric motor; 15 – millivoltmeter; 16 – reduction valve; 17 – filter of preliminary purification.

*Bashkir Scientific Research Institute of Oil Refining.

is possible to investigate, besides the remaining factors, the effect of ullage on the filterability of fuels. The fundamental diagram of the installation is shown in Fig. 32. The tested fuel is passed from the tank through a filter of preliminary purification to a heat exchanger, in which occurs heating of fuel by a flow of hot air proceeding from a three-sectional heating furnace. The heated fuel, under pressure of gas, passes through a filter, is cooled and is run off.

On an installation developed at VNII NP [All-Union Scientific Research Institute for Oil and Gas Refining and Production of Synthetic Liquid Fuel] [55] an attempt was made to estimate the stability of fuels during heating by circulatory flow through pumps of jet engines (Fig. 33). Fuels were tested on a stand and in a thermostat. The test consists in circulatory pumping of fuel (60 liters) by eight-hour stages at a temperature on the pump inlet of +50°C. Every stage is divided into two half-stages with an interval between them sufficient for cooling the fuel to the ambient temperature. Every 8 hr the fuel is replaced with fresh; over the entire test period (25 stages) 1500 liters are expended. In intervals between stages (5-7 days) the pumps are filled with the tested fuel and held in a thermostat at a temperature of +40°C. During the test the quality of fuel is systematically controlled, basically by the change in the content of existent gums. After 50, 100, and [illegible] hr of test the pumps are subjected to partial disassembly and inspection. Special attention is paid to the presence on components of sediment and deposits of gums. The total maximum duration of the test of one sample of fuel

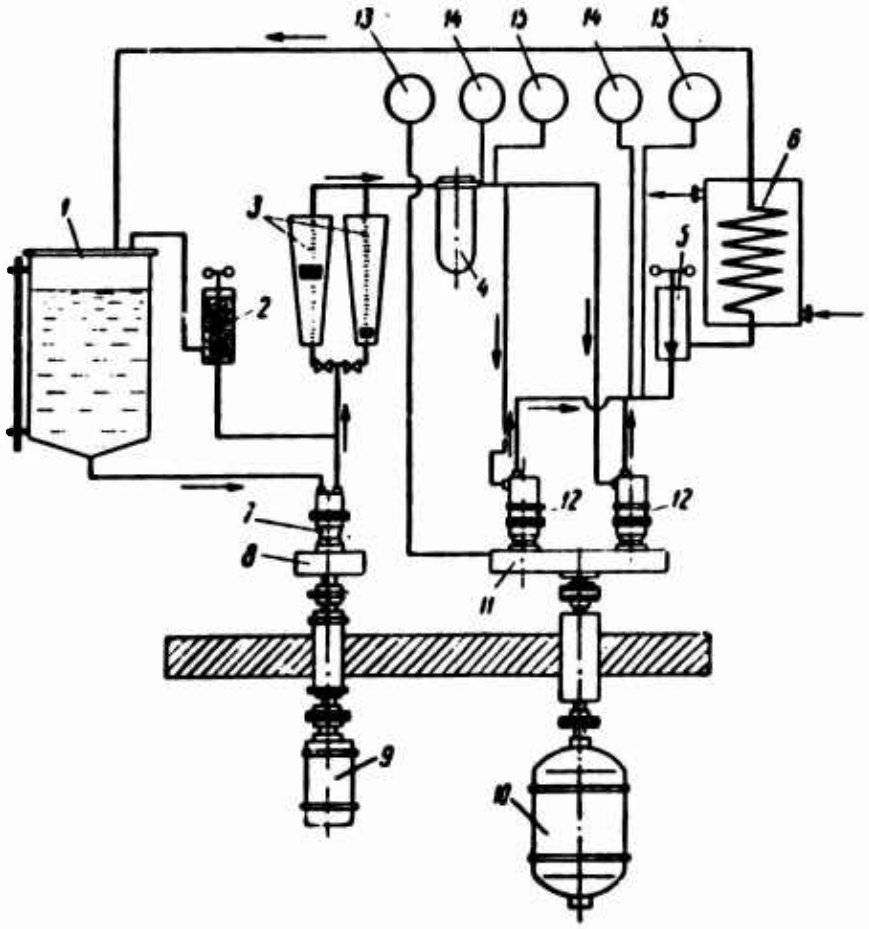

Fig. 33. Fundamental diagram of installation with fuel pump of turbojet engine for testing fuel for circulatory flow. 1 — tank for fuel; 2 — valve of bypass; 3 — float-type flowmeters; 4 — filter; 5 — choke cock; 6 — cooler; 7 — fuel booster pump; 8 — reductor; 9, 10 — electric motors; 11 — reductor; 12 — fuel pumps of high pressure; 13 — tachometer; 14 — manometer; 15 — thermocouple.

(6 months) is comparable to the actual calendar period of operation of an engine.

The pumpability of jet fuels at raised temperatures depends on temperature, time of circulation, chemical composition of fuel, concentration of oxygen, contact with various metals from which the fuel system is made, and other factors.

On the installation [52] fuels T-5, T-1 and TS-1 were tested. Figures 34-36 give data on the filterability of these jet fuels in various conditions. As can be seen from the given data, all the fuels have the poorest filterability in a certain region of temperatures: for T-5, 160-190°C; T-1, 140-150°C; TS-1, 160°C.

With increase and lowering of temperature the filterability of fuels is considerably improved. This is explained by the fact that for every fuel there exists a certain temperature zone at which maximum sedimentation is observed [26, 54]. Of the fuels T-1, TS-1, and T-5, fuel T-5 has the poorest filterability. As early or after 30 minutes of operation of the installation at 180-190°C the pressure drop on the filter attains 400 mm Hg. The same pressure drop is attained at the temperature of maximum sedimentation for fuel TS-1 after 2 hr and for fuel T-1, after 3 hr of operation. The poor filterability of fuel T-5 is explained by the fact that with an increase in the molecular weight of fuels their stability drops and during heating in identical conditions more sediment and insoluble tars will be formed in such fuels.

Fuels T-5 and TS-1 filter well to a temperature of 140°C (Figs. 34, 35) and

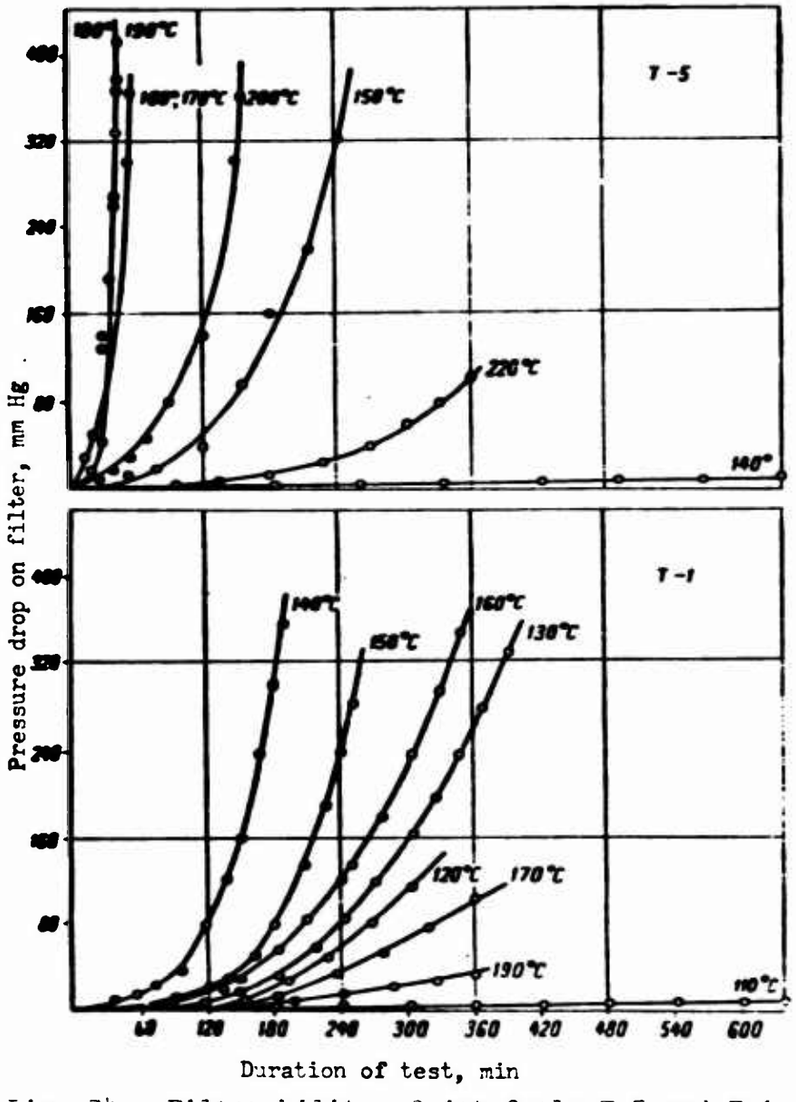

Fig. 34. Filterability of jet fuels T-5 and T-1 at various temperatures.

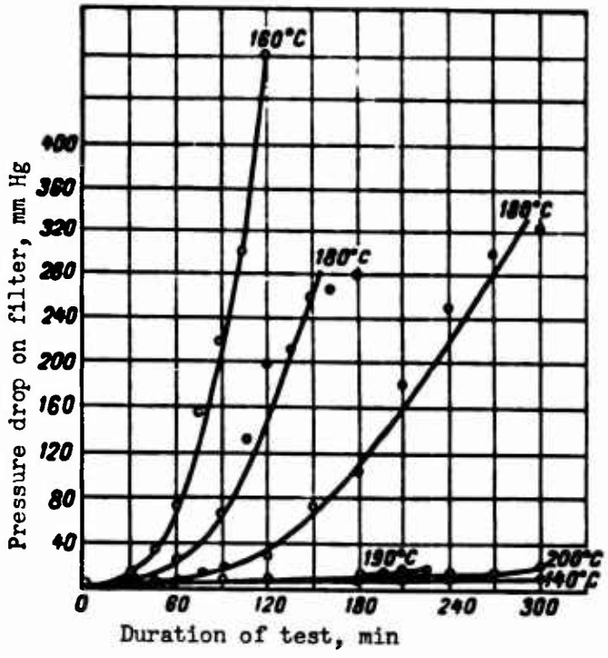

Fig. 35. Filterability of fuel TS-1 at various temperatures.

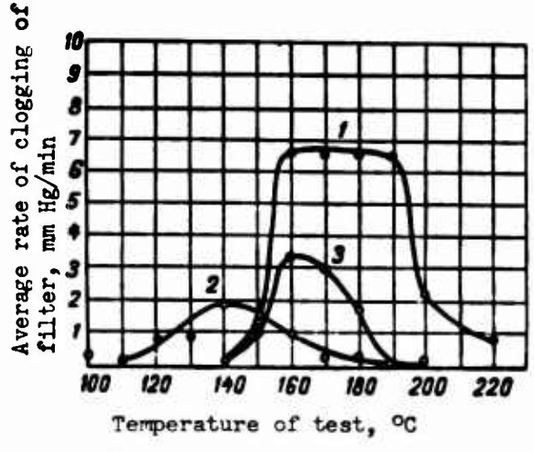

Fig. 36. Dependence of average rate of clogging of filter on test temperature. 1 — fuel T-5; 2 — fuel T-1; 3 — fuel TS-1.

fuel T-1 to a temperature of 110°C (Fig. 34). With a further increase in temperature the filterability of the fuels worsens and after the fuel is heated higher than the "dangerous zone" the filterability of the fuels again improves. Thus, if it were possible to heat the fuel rapidly above a certain temperature, it would be possible to avoid maximum sedimentation. However, in practice this is difficult to carry out, inasmuch as heating of fuel in aircraft occurs gradually over a certain period of time.

The filterability of jet fuels at high t mperatures depends on their chemical composition. A negative influence on fuel filterability is rendered by aromatic bicyclic, aromatics with unsaturated side chains, and unsaturated hydrocarbons and also by various heterocrganic compounds.

Of the individual hydrocarbons investigated [69], the poorest filterability was shown by bicyclic aromatic hydrocarbons (Fig. 37). Aliphatic hydrocarbons have best filterability. It is necessary to note that pure unsaturated hydrocarbons have good filterability (Fig. 37); however, with heating a fuel with components of thermal cracking will form much sediment and has poor filterability (Fig. 38).

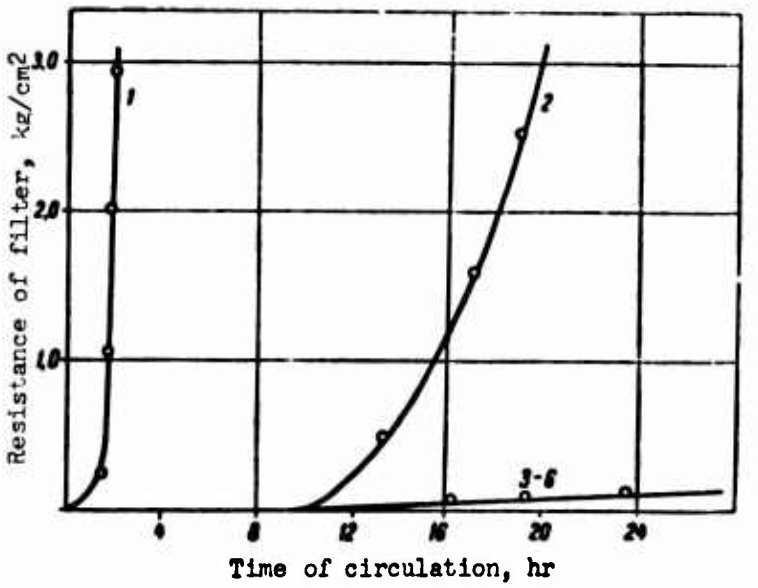

Fig. 37. Filterability of certain individual hydrocarbons. 1 — α-methylnapthalene; 2 — tetralin; 3 — cis-decalin; 4 — dodecane; 5 — dodecene-1; 6 — cetene.

During investigation [56] of the filterability of fuel T-2 with addition of components of thermal cracking (Fig. 39) it was established that the pressure drop on the fuel filter of the installation with real aggregates at 150°C attains 600 mm Hg after as little as 60 minutes of operation.

The poor filterability of fuels which contain unsaturated hydrocarbons is explained by the fact that during heating the unsaturated hydrocarbons are quickly oxidized, with subsequent formation of considerable quantities of insoluble gums and sediments which clog fuel filters.

Among the heteroorganic compounds, the greatest influence on filterability is rendered by sulfur compounds and tarry substances. Of the sulfur compounds, definitely, th mercaptans and also elemental sulfur have the greatest effect on

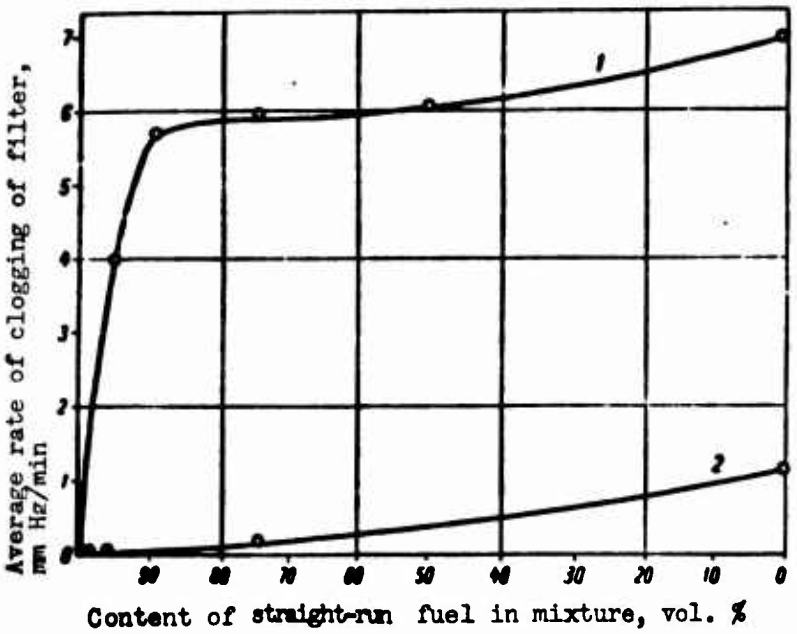

Fig. 38. Influence of unsaturated hydrocarbons and formed tars on the filterability of fuel of straight run distillation. 1 — fuel from cracking kerosene; 2 — fuel from the hydrocarbon fraction of cracking kerosene.

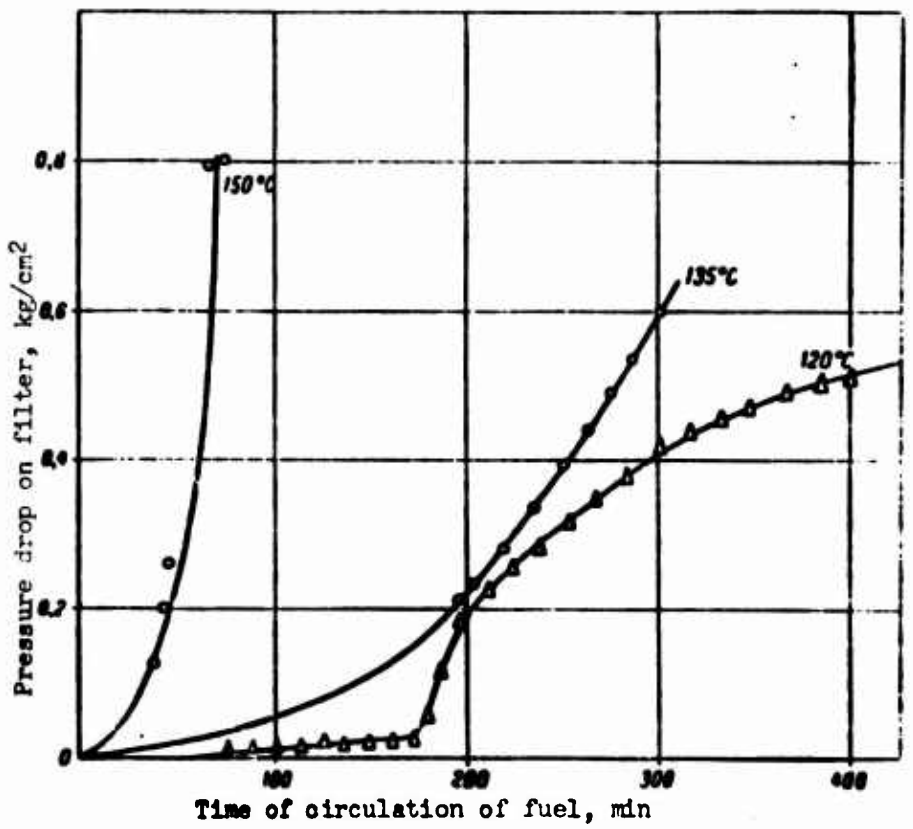

Fig. 39. Filterability of fuel T-2 with addition of components of thermal cracking.

filterability. With an increase in the content of mercaptans the filterability of fuels sharply worsens (Fig. 40); this is explained by the intense sedimentation of fuels containing mercaptans during heating [26].

Tarry substances, as a rule, also worsen the filterability of fuels during heating. Z. A. Sablina and A. A. Gureyev [59] separated tarry substances from kerosene by chromatographic means on activated oxide of aluminum. The characteristics of tarry substances are given in Table 40. Tarry substances were added to the hydrocarbon part of the fuel and to the parent fuel in various concentrations and then these mixtures were tested on a pumping installation [52].

With an increase in the content of tarry compounds in fuels and hydrocarbon fractions there is observed a considerable impairment of their filterability (Fig. 41). However, complete removal from fuel of tarry substances is inexpedient, inasmuch as in optimum quantities (0.04 to 0.06 wt.%) natural tarry substances can retard oxidation of fuels [60].

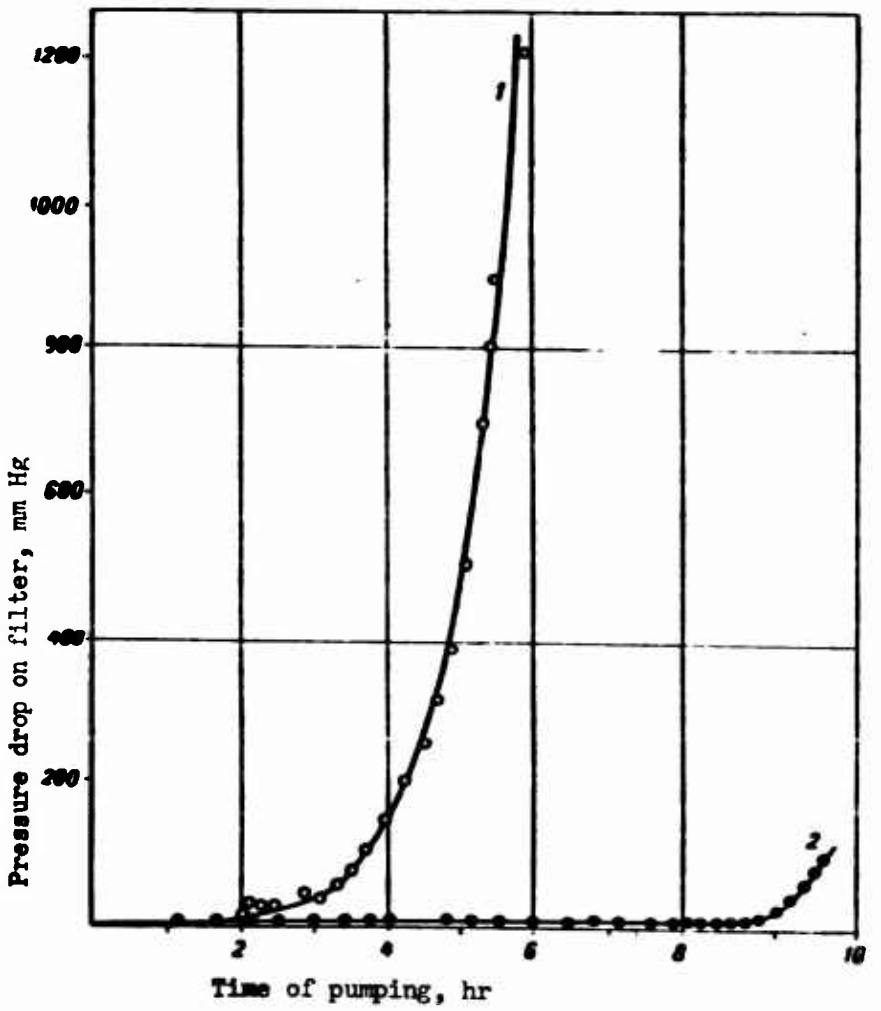

Fig. 40. Influence of mercaptans on filterability of sulfurous jet fuels at a temperature of 120°C [56, 58]. 1 — fuel TS-1 with 0.045% mercaptan sulfur; 2 — fuel TS-1 with 0.002% mercaptan sulfur.

Table 40. Tarry Compounds Separated from Fuels of Various Types

Fuel	Quantity of tarry compounds, mg/100 ml	Density ρ_4^{20}, g/cm³	Molecular weight	Acid number, mg KOH/gram	Iodine number, g iodine/100 g	Composition by elements			
						C	H	S	O+N
Kerosene, straight run distillation, from low-sulfur crudes	35	1,0052	169	1,99	142	76,8	9,8	10,0	3,4
Lightened kerosene, straight run distillation, from sulfurous crudes	23	0,9591	148	12,0	119	73,7	10,2	6,8	9,3
Kerosene gas oil fractions, straight run distillation, from low-sulfur crudes	60	0,9865	156	4,4	87	79,8	10,3	1,4	8,5
Kerosene of thermal cracking from sulfurous crudes	300	1,0257	193	8,5	165	—	—	—	—
Gas oil of catalytical cracking from low-sulfur crudes	150	—	225	56,5	107	79,5	9,4	0,7	10,4

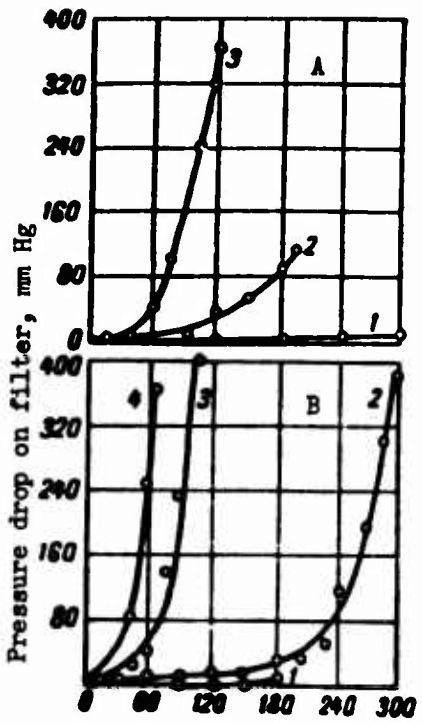

Fig. 41. Influence of tarry substances on filterability of fuels at a temperature of 110 (A) and 180°C (B). 1A — kerosene from sulfur-free crude; 1B — hydrocarbon part of lightened kerosene (type T-2) from sulfurous crudes; 2 — the same, with addition of tarry substances of 10 mg/100 ml; 3 — the same, +19 mg/100 ml; 4 — the same, +138 mg/100 ml.

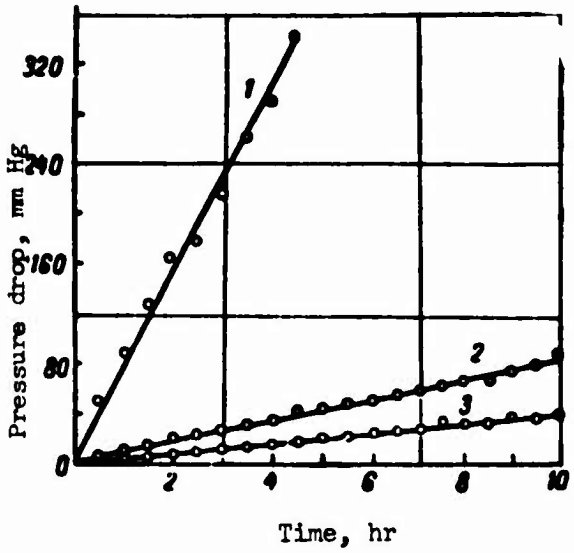

Fig. 42. Influence of gaseous environment on filterability of fuel TS-1. 1 — in medium of air at 150°C; 2 — in medium of nitrogen (impurity 5% O_2) at 150°C; 3 — under pressure of its own vapor at 200°C.

Inasmuch as the filterability of fuels at high temperatures depends on the formed products of oxidation and their consolidation, it is fully natural to expect that in medium of inert gases filterability of fuels will be considerably improved. Investigations conducted at BashNII NP confirmed this position [13]. For the investigations they took the commercial fuel TS-1, which was investigated in media of air, nitrogen, and its own vapor. During contact of the fuel with air it shows the poorest filterability (Fig. 42). In the absence of oxygen the filterability of fuel becomes satisfactory with heating for 10 hours. Thus, once again it is confirmed that the formation of sediment is a consequence of oxidizing processes proceeding in fuels during heating.

Improvement of Filterability of Fuels at High Temperatures

There exist the following ways to improve the filterability of fuels at high temperatures:

– purification of fuels of unstable components;

– thorough filtration of fuels before refueling aircraft. Mechanical impurities with dimensions down to 2-3 μ must be removed;

– application of additives which prevent sediment and gum formation in fuels during heating;

– removal of air from fuel system and its replacement with an inert gas.

The following methods of purification have been proposed: sulfuric acid, selective, absorptive, hydrogenation, and others.

With passage through activated aluminum oxide [47, 59] and after purification by concentrated sulfuric acid [51] the filterability of fuels was improved by several times. A study was made of fuel filterability after purification by sulfurous anhydride [1]. Although the filterability of fuels was improved, it is considered that this method of purification is not quite acceptable [1].

The most promising is the application of hydropurification, especially if one considers that the obtaining of hydrogen in contemporary conditions does not present difficulties [1, 62, 63].

For the purpose of obtaining high-quality fuels for supersonic aviation the method of catalytical cracking in presence of hydrogen – hydrocracking – is proposed [1, 47-50, 61].

Jet fuel obtained through hydrocracking [1] has (at high temperatures) better filterability than analogous fuel obtained by method of straight run distillation (Fig. 43). With an increase in the depth of purification of sulfur and also in the degree of hydrogenation of aromatic hydrocarbons, the filterability of fuels is increased (Table 41). Besides good filterability, at high temperatures these fuels have high density and large heat of combustion [63].

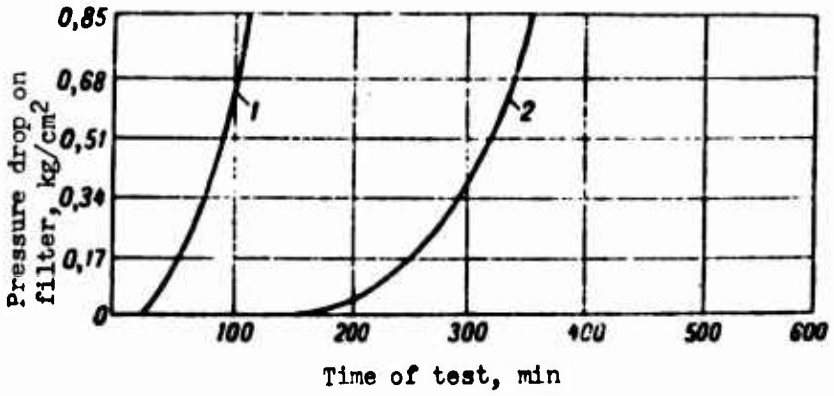

Fig. 43. Filterability of fuels of straight-run distillation and hydrocracking at a temperature of 200°C on the CFR installation [50]. 1 – fuel of straight-run distillation; 2 – fuel of hydrocracking.

Table 41. Influence of Degree of Hydrogenation on Filterability of Aromatic Concentrates* [63]

Indices	Quantity of nonreacting aromatic hydrocarbons, vol. %			
	1	12	17	21
Content of sulfur in hydrogenate, %	0.001	0.033	0.020	0.056
Filterability of fuels:				
time of test, min	300	300	300	125
pressure drop on filter, mm Hg	5	405	200	625

*During tests a temperature of 232°C was maintained in the heater and on the filter, 260°C.

The filterability of jet fuels at raised temperatures is greatly influenced by preliminary purification of the fuel from mechanical impurities [70]. We speak not only of these mechanical impurities whose absence is controlled in accordance with GOST's, but also of microimpurities, not visible to the naked eye. During heating of fuels complicated processes occur, connected in the first place with oxidation of unstable components of the fuel and leading to the formation of a solid phase. The formation of the solid phase (sediment) is influenced by microcontaminations existing in the fuel [18, 71]. Removal from the fuel of particles with dimensions less than 20-15 μ leads to a considerable decrease in sedimentation and consequently to improvement of fuel filterability.

The filterability of fuels can be considerably improved with help of additives. Additives for improving filterability of fuels at raised temperatures must be:

– anticorrosive, in order to protect metal in fuel from destruction and to prevent formation in fuels of gums and sediment;

– antioxidant, in order to prevent development of processes of oxidation of fuels;

– dispersive, in order to prevent enlargement of particles of insoluble sediment to dimensions exceeding those of the holes of filtering elements of the fuel system of the engine.

The majority of existing additives are unsuitable for increasing stability of fuels at raised temperatures. In USSR and abroad boundary new additives are being created which well improve filterability of jet fuels at raised temperatures [40, 42, 60, 64, 65, 66].

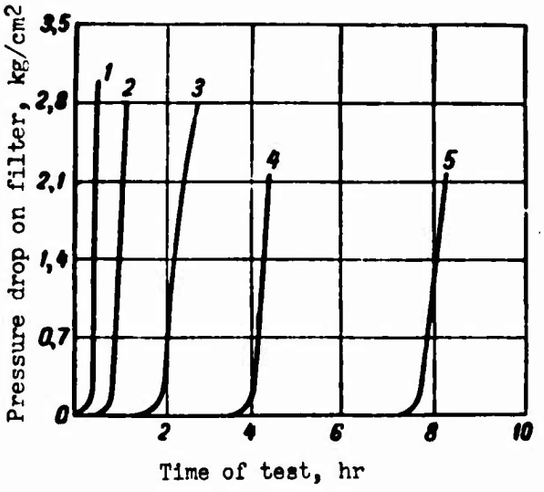

Fig. 44. Influence of dispersive additives on filterability of jet fuel. 1 — parent fuel without additives; 2 — with best antioxidant; 3 — with dispersive additive "A"; 4 — with dispersive additive "B"; 5 — with dispersive additive "C."

The most effective additives are the ashless additives of the type of polar polymers [67, 68], whose composition includes nitrogen bases, certain compounds containing amine, thiol, and phenyl groups [60, 64] and also certain amines, quinols, and imedazols [64, 66].

Figure 44 shows the influence [65] of certain antioxidant and dispersive additives on the filterability of jet fuels on the CFR installation [50]. One can see that purely antioxidant additives do not ensure filterability of jet fuels; dispersive additions possess somewhat better properties. Obviously the best additives will be multifunctional, having anticorrosive, antioxidant, and dispersive properties.

Pumpability of Jet Fuels at Great Altitudes

With an increase in flight altitude of aircraft there occurs a decrease in atomospheric pressure. Thus, for instance, at 18 km the pressure is 60 mm Hg. With a decrease in external pressure the volatility of fuels will increase; conditions for separation from the fuel of dissolved air and other gases are improved. The liberated gases and vapors collect in different places of the fuel system (in booster pump, bends of fuel lines, and others). The appearance of vapor locks leads to a decrease in pressure and flow rate of fuel, to disturbance or normal operation of the fuel pump. Vapor locks appear most easily in the suction lines of the booster pump. The limiting vacuumetric height of suction of pump is equal to

$$H_в = \frac{p_a}{\rho_4^t} - p_s,$$

[в = vac = vacuumetric]

where H_{vac} is the limiting vacuumetric height of suction, mm Hg;

p_a is atmospheric pressure, mm Hg;

ρ_4^t is the relative density of the liquid;

p_s is the pressure of saturated vapor of pumped liquid, mm Hg.

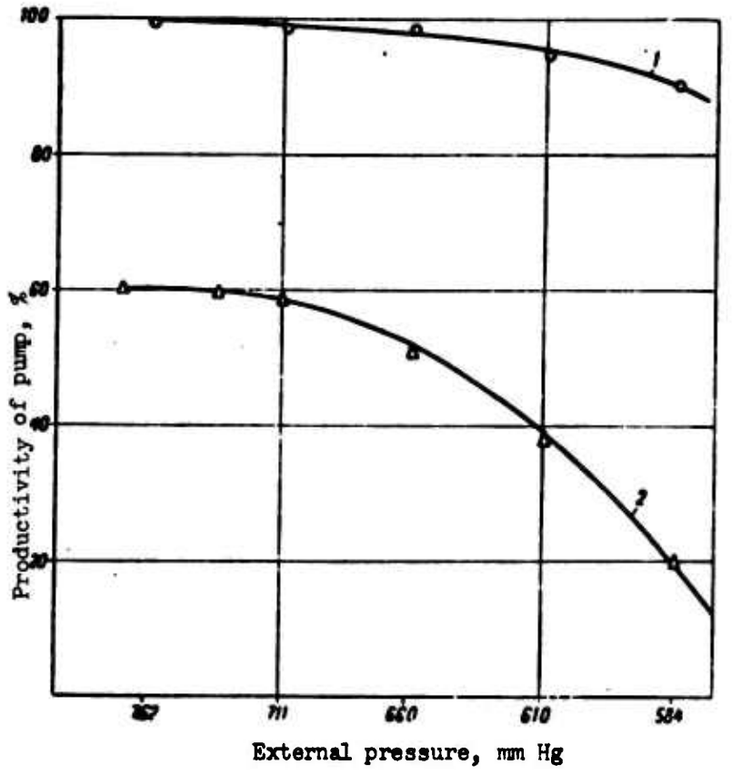

Fig. 45. Change in productivity of fuel pump, depending upon the vapor pressure of the fuel. 1 — vapor pressure 2 mm Hg; 2 — vapor pressure 360 mm Hg.

With a decrease in the difference $\frac{p_a}{\rho} - p_s$, vapors and gases proceed to the pump together with the fuel, normal flow is disturbed, and the quantity of fuel moved decreases. Theoretically fuel feed ceases when $\frac{p_a}{\rho} = p_s$. If one were to consider the flow friction of the sucking pipeline, cessation of fuel feed to pump will occur before the pressure of saturated vapor reaches the value $\frac{p_a}{\rho}$. With strong vaporization, there is moved over the line not a solid fluid flow, but a mixture of fuel with vapors and gases. Owing to the compressibility of such a mixture there appears pulsation of pressure in the fuel system and lowering of supply pressure.

With an increase in altitude and in the pressure of saturated vapor of fuel, productivity of the pump sharply decreases (Fig. 45). With an increase in the pressure of saturated fuel vapors, the permissible altitude of the aircraft decreases (Fig. 46).

Thus, for instance, if the temperature of the fuel in the fuel system of an aircraft equals +20°C and the pressure of the saturated vapor at 38°C is equal to 760 mm Hg, in this fuel stormy liberation of a vapor-gas mixture will begin at 19 km. However, the same fuel at a temperature of +10°C will "boil" at 21 km. The pressure of saturated vapor increases intensely with heating of fuels in aircraft at supersonic speeds.

Inclination of fuels to the formation of vapor locks can be determined by the ratio of the volumes of the liquid and vapor phases. It has been established that the formation of vapor locks disturbs normal engine operation if $(V_{vap}/V_{liq}) > 2$, where V_{vap} is the volume of the vapor phase; V_{liq} is the volume of the liquid phase. Table 42 shows the effect of flight altitude on the ratio V_{vap}/V_{liq}.

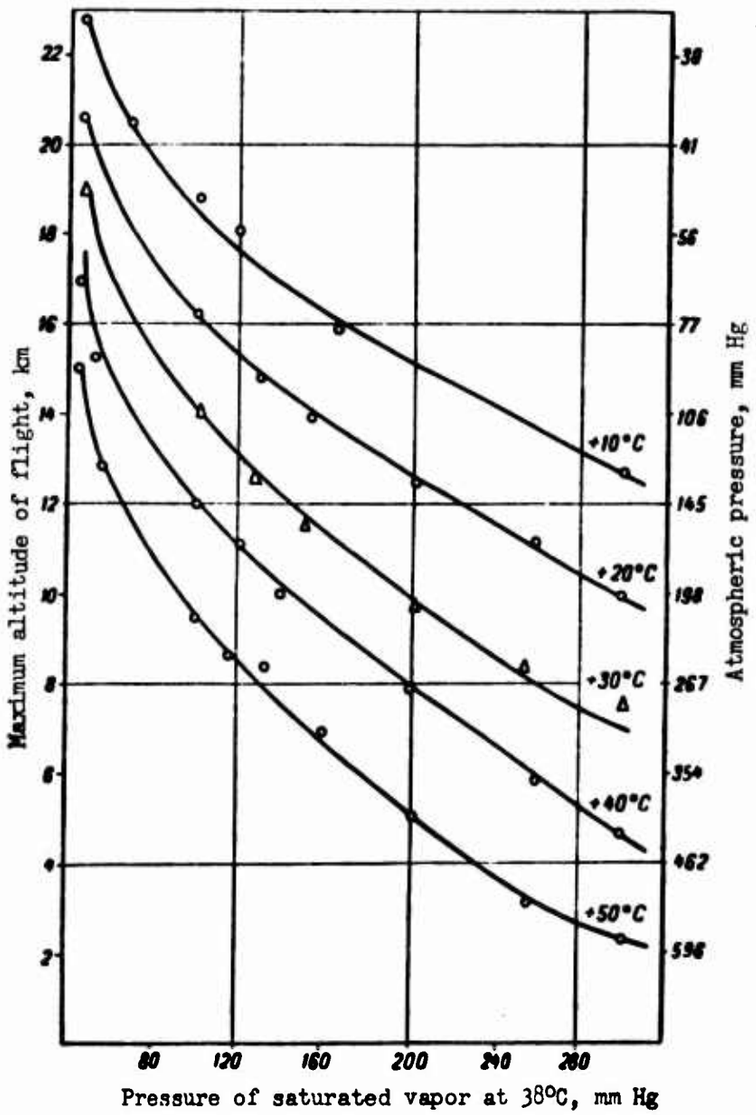

Fig. 46. Influence of pressure of saturated vapor and temperature on maximum altitude of flight.

Table 42. Effect of Flight Altitude on the Ratio of Vapor and Liquid Phases at 38°C

Fuel	Ratio V_{vap}/V_{liq} at altitude of (km)					
	3.0	4.6	5.0	9.0	12.0	16.7
T-1	0.1	0.1	0.2	0.4	1.0	2.0
T-2	0.4	0.8	1.0	1.3	2.0	9.0

Table 43. Removal of "Boiling" and Losses of Fuel by Cooling or by Creation of Excess Pressure in Tanks of Aircraft During Ascent to a Height of 18 km [3]

Fuel and its temperature in °C	Loss of fuel, wt. %		Excess pressure necessary in tanks for removal of boiling and losses, mm Hg	Temperature necessary for removal of boiling and losses, °C, not above
	Tanks without pressure	Tanks under excess pressure of 100 mm Hg		
Wide fractional composition with pressure of saturated vapors of 350 mm Hg:				
15.5	9.6	0	80	-
37.8	15.0	5.8	235	-23
Wide fractional composition with vapor pressure of 100 mm Hg				
15.5	0	0	0	-
37.8	1.0	0	10	+30

From the table it follows that at a fuel temperature of +38°C normal operation of fuel pumps on fuel T-1 is disturbed at a height of approximately 17 km, and on fuel T-2 at a height of the order of 12 km.

The formation of vapor locks can be decreased by operation of the fuel system under pressure, by cooling of the fuel before flight (Table 43), and by certain other measures.

The necessary excess pressure which must be created to prevent the formation of vapor locks is determined by the difference between the pressure of saturated vapor of the fuel at a given temperature and atmospheric pressure. However, an increase of pressure in the fuel system makes it necessary to establish additional equipment on the aircraft and increases its gross weight. Preliminary cooling of fuel is easier and besides decreasing the pressure of saturated vapor of fuel, it permits increasing the quantity of fuel loaded in the fuel tanks.

Fuels T-1 and TS-1 have low pressure of saturated vapor and ensure normal flight without excess pressure in tanks at heights up to 18-20 km; fuel T-5 ensures normal flight at still greater heights.

The inclination of fuel to form air locks is greatly influenced by air dissolved in the fuel. The solubility of air in fuel depends on external pressure. During a climb air dissolved in the fuel starts to be liberated and can lead to disturbances of pumpability of fuels (Table 44).

Table 44. Liberation of Air Dissolved in Fuels During Climb [73]

Height of flight, km	Atmospheric pressure, mm Hg	Quantity of air liberated from fuel, vol. %				Content of air in fuel, vol. %	
		Fuel of type T-1		Fuel of type T-2			
		on climb	incremental total	on climb	incremental total	Fuel of type T-1	Fuel of type T-2
0	760	0	0	0	0	11,5	18,5
0,7	700	6,1	6,1	5,4	5,4	10,8	17,5
1,8	600	15 6	21,7	13,5	18,9	9,0	15,0
3,4	500	13,0	34,7	13,5	32,4	7,5	12,5
5,3	400	13.0	47,7	13.5	45,9	6,0	10,0
7,2	300	13,0	60,7	20,8	66,7	4.5	6.0
10,0	200	13,0	73,7	5,4	72.1	3,0	5,0
14,2	100	10,4	84,1	13,5	85,6	1,8	2,5
22,0	30	13,9	98,0	10,3	95,9	0,2	0,6

As can be seen from the given data, during ascent to a height of 22 km almost all the air contained in fuels is liberated. The liberated air occupies a considerable volume. For instance, with a tank capacity of 30 m^3 the volume of liberated air will be about 5 m^3. This air escapes through drain system, removing with itself fuel vapors, and may cause disturbance of normal fuel feed in the fuel system.

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C H A P T E R VI

THERMOOXIDIZING STABILITY AND ANTIWEAR PROPERTIES OF JET FUELS

In connection with the increase in speed and range of aircraft new requirements for quality of fuels have appeared. The most essential requirement consists in the necessity of an increase in stability and decrease of corrosivity of fuels at raised temperatures, i.e., the need for increased thermooxidizing stability of fuels.

Due to insufficient thermooxidizing stability of fuels during heating, gums and sediment formed in them are deposited on filters, walls of fuel lines, and friction parts of the fuel system; this causes disturbance of normal engine operation. For instance, disturbance of the work of the filter and command aggregate causes a drop in thrust. Impairment of atomization of fuel by injectors causes disturbance of normal conditions of combustion in the chambers; as a consequence, scale information is increased, provoking warping and burnt spots on the walls of the chamber and the blades of the turbine.

Conditions and Causes of Formation of Insoluble Sediment and Gum During Heating of Jet Fuels

As was already noted, during heating of jet fuels there occurs formation of insoluble sediment and gums. This problem arose with the appearance of supersonic aircraft. In order essentially to limit the formation of sediment and gums or, in other words, to increase thermooxidizing stability of fuels, it is necessary to study the causes and conditions of formation of the second [the solid] phase in fuels during heating.

The stability of fuels and their corrosivity at raised temperatures are influenced by conditions of heating (temperature, pressure, concentration of oxygen, contact with

metals) and by the chemical composition of the fuels.

Influence of Temperature and Pressure

With an increase in temperature there first occurs an increase in the quantity of sediment formed, which attains a maximum at a certain temperature (140-170°C). With a further increase in temperature [5, 24, 25] the quantity of sediment formed decreases (Fig. 47).

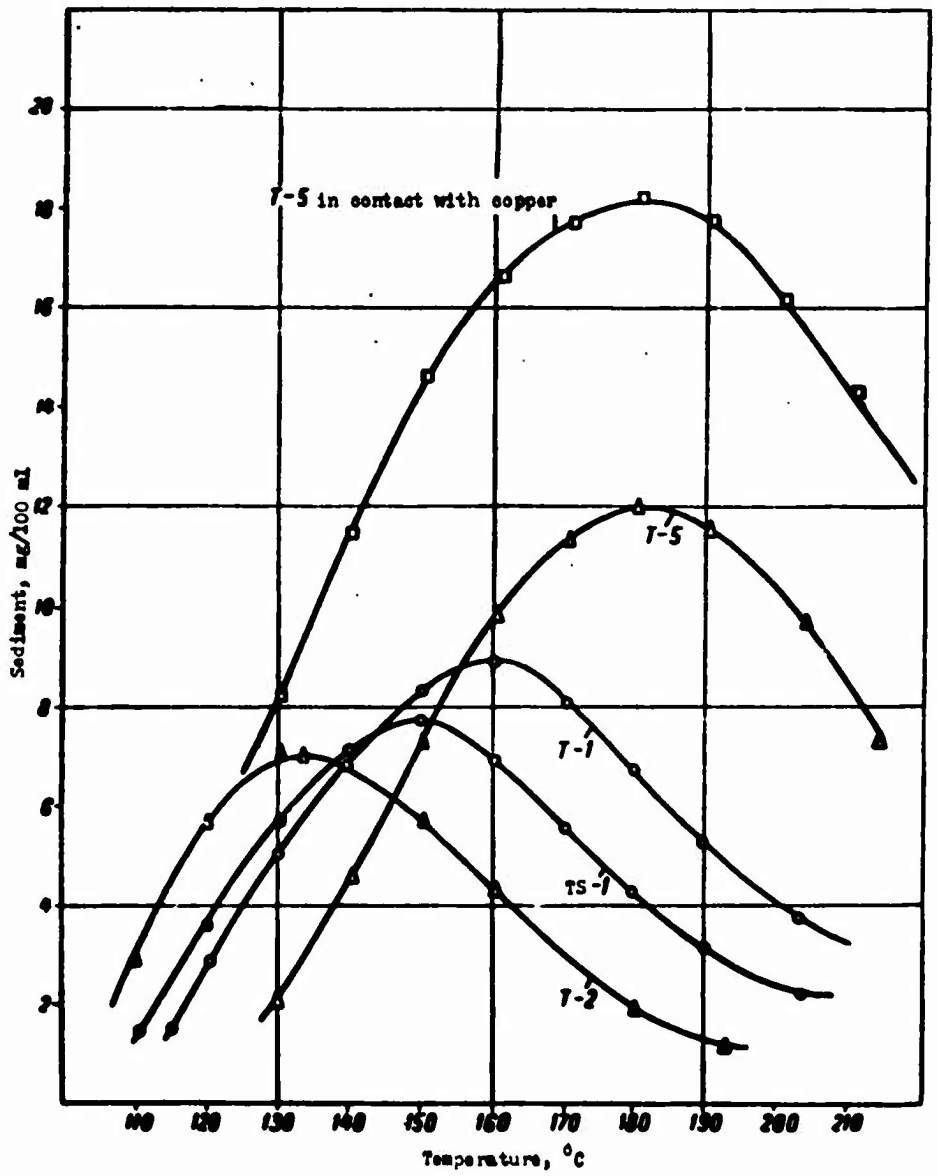

Fig. 47. Influence of temperature on formation of insoluble sediment in jet fuels.

The maximum of sedimentation can be explained as follows. At temperatures less than 120°C oxidation of fuel in the liquid phase occurs at relatively low rates; it does not lead to considerable formation of insoluble sediment. With an increase in temperature the rate of oxidation increases; this causes an increase in the formation of sediment. However, with a further increase in temperature once more

there is observed a decrease in sedimentation. It is necessary to note that the rate of oxidation is influenced not only by temperature but also by the concentration of oxygen, both dissolved in the fuel and located in the ullage above the fuel. An increase in temperature leads to a decrease in the solubility of oxygen in the fuel and also prevents its penetration into fuel, owing to the increase in the vapor pressure of the fuel. Thus the oxidation of low-stability components of fuels will be intensified only up to a temperature at which the vapor pressure sharply increases. Layer of vapor (both in static and in dynamic conditions) reliably "screens" the fuel from oxygen [21]. It has been established that without oxygen there is no sedimentation [14, 15].

Every fuel is characterized by its temperature of equilibrium boiling (Table 45). Depending upon this, the temperatures of maximum sedimentation, which lie in the region of temperatures of equilibrium boiling of the fuels, can be established.

Table 45. Change in Temperature of Equilibrium Boiling of Fuels, Depending upon Pressure Developed During Heating

Fuels	At normal pressure		At raised pressure			
	Limits of evaporation, °C	Temperature of equilibrium boiling, °C	Temperature of heating, °C	Pressure over the fuel, atm	Limits of boiling under pressure, °C	Temperature of equilibrium boiling under pressure, °C
T-2	62—237	116,6	120 150 200 250	2,20 2,85 4,85 8,00	85 -200 105—310 130—345 154—380	147 160 190 214
TS-1	137—226	164,6	120 150 200 250	1,55 1,90 2,70 4,95	155—243 164—256 176—270 205—305	183 190 205 236
T-1	143—267	178,8	120 150 200 250	1,45 1,85 2,35 4,30	157—284 170—298 185—315 205—345	188 202 208 242
T-5	186—306	233,9	120 150 200 250	1,25 1,40 1,80 2,65	195—316 200—330 210—330 230—380	245 250 258 280

For heavier fuels the temperature of maximum sedimentation will be displaced into the region of higher temperatures. This is confirmed by experimental data (Fig. 47). With an increase in temperature increase in the coarseness particles of sediment formed in jet fuels is observed (Table 46).

Table 46. Influence of Temperature on Particle Size of Insoluble Sediment Formed in Jet Fuels During Heating [14]

Temperature °C	Total weight of sediment on No 4 glass filter, mg/100 ml	Sediment on filters % of total weight of sediment				
		5—7μ	15μ	30μ	50μ	120 μ
		Fuel T-5				
120	1,9	81,5	28,4	5,2	0	0
150	4,9	94,0	61	33,4	26	4
200	0,6	100	100	100	54	38,5
250	0,4	100	100	100	63,4	44,4
		Fuel T-1				
120	5,2	70	24	2,3	0	0
150	7,5	9,75	74,6	47,1	30,7	13,6
200	2,0	100	100	100	47,5	15,0
250	1,7	100	100	100	53	18,0
		Fuel TS-1				
120	3,4	61	24,6	2,9	0	0
150	6,9	97	63	47,7	34	8
200	1,3	100	100	100	44,4	15
250	1,0	100	100	100	60	30

It is interesting to note that starting from a temperature of 200°C, no particles with a dimension less than 50 μ are formed in fuel.

With an increase in total pressure (at identical oxygen concentration) no considerable change in the formation of sediment is observed [14]. The particle size of the formed sediment is also unchanged.

Influence of Composition of Gaseous Environment

The formation in fuels during heating of insoluble and soluble products of oxidation is connected first of all with the presence of oxygen, both dissolved in the fuel and also in the gaseous environment over the fuel. With a decrease of the oxygen in the gaseous environment, sediment and gum formation in fuels decreases sharply (Table 47).

Table 47. Influence of Gaseous Environment on Formation of Insoluble Sediment in Fuels

Temperature, °C	Fuels			
	T-5	TC	T-1	T-2
	In atmosphere of air			
125	4,5	3,2	3,8	2,0
150	10,1	13,7	14,0	9,1
200	5,0	6,3	7,0	3,4
250	1,3	4,3	5,2	1,9
	In atmosphere of nitrogen of containing 1.2 % oxygen			
125	0,1	0,7	0,6	0,2
150	0,6	1,2	1,4	0,2
200	0,2	0,8	0,9	0,2
250	0,1	0,4	0,6	0,1

It has been shown [15] that with a decrease in the concentration of oxygen there is a decrease in the inclination of fuel to oxidation (Fig. 48) and to the formation of insoluble sediment (Fig. 49).

As can be seen from these data, at an oxygen concentration up to 50 g/m^3 sedimentation decreases more by more

than 10 times as compared to that with a concentration of oxygen of 288 g/m^3 (this corresponds to the composition of air at the earth's surface).

These data are direct confirmation of the fact that the formation of sediment is the result of the development of processes of oxidation of fuels.

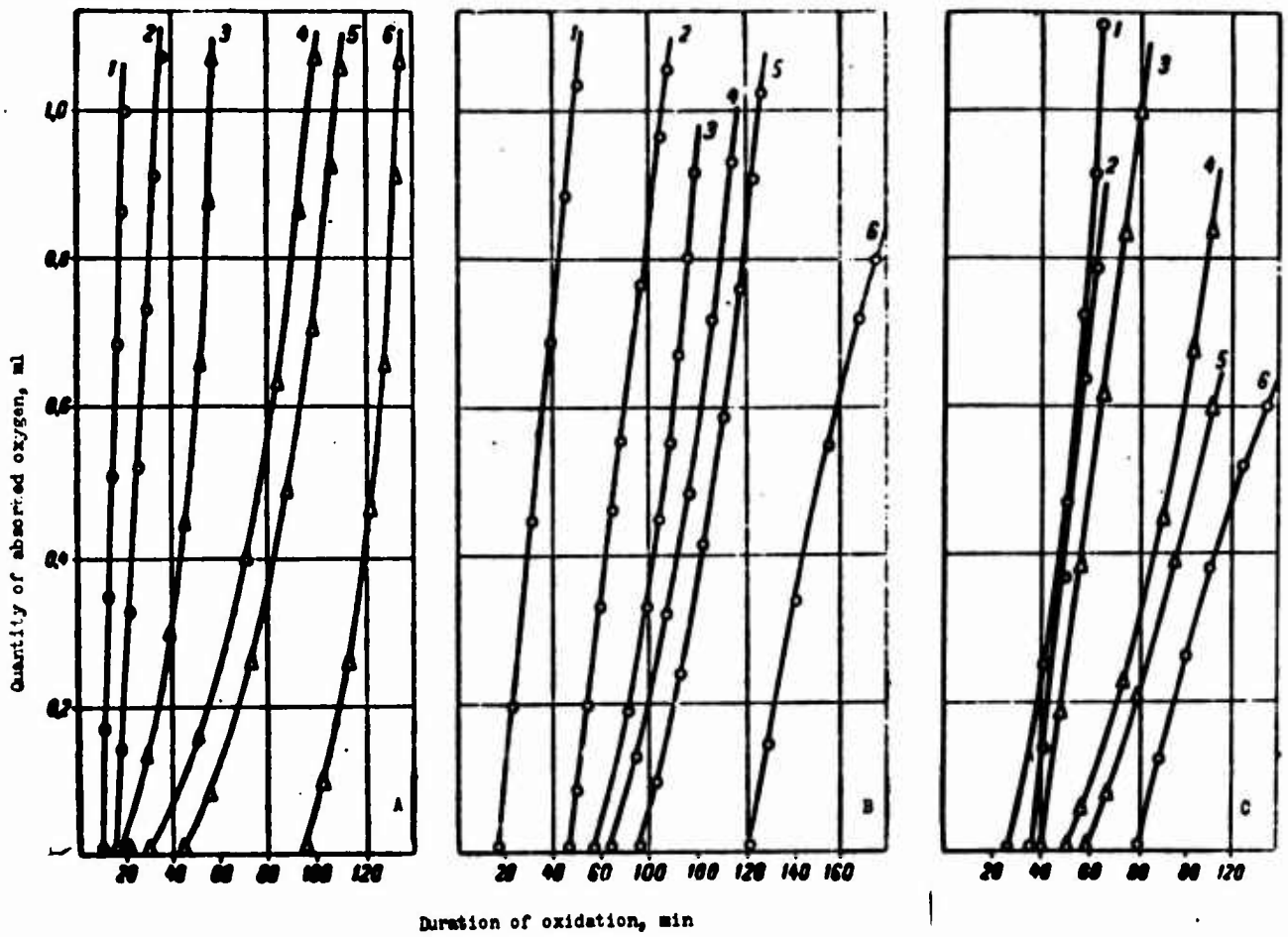

Fig. 48. Influence of concentration of oxygen on rate of oxidation of jet fuels T-2 (A), T-1 (B), and TS-1 (C) at 150°C in contact with VB-24N bronze. 1 – in atmosphere of oxygen; 2 – concentration of oxygen in air, 288 g/m^3; 3 – concentration of oxygen, 89.7 g/m^3; 4 – concentration of oxygen 47.5 g/m^3; 5 – concentration of oxygen 17.3 g/m^3; 6 – concentration of oxygen 6.6 g/m^3.

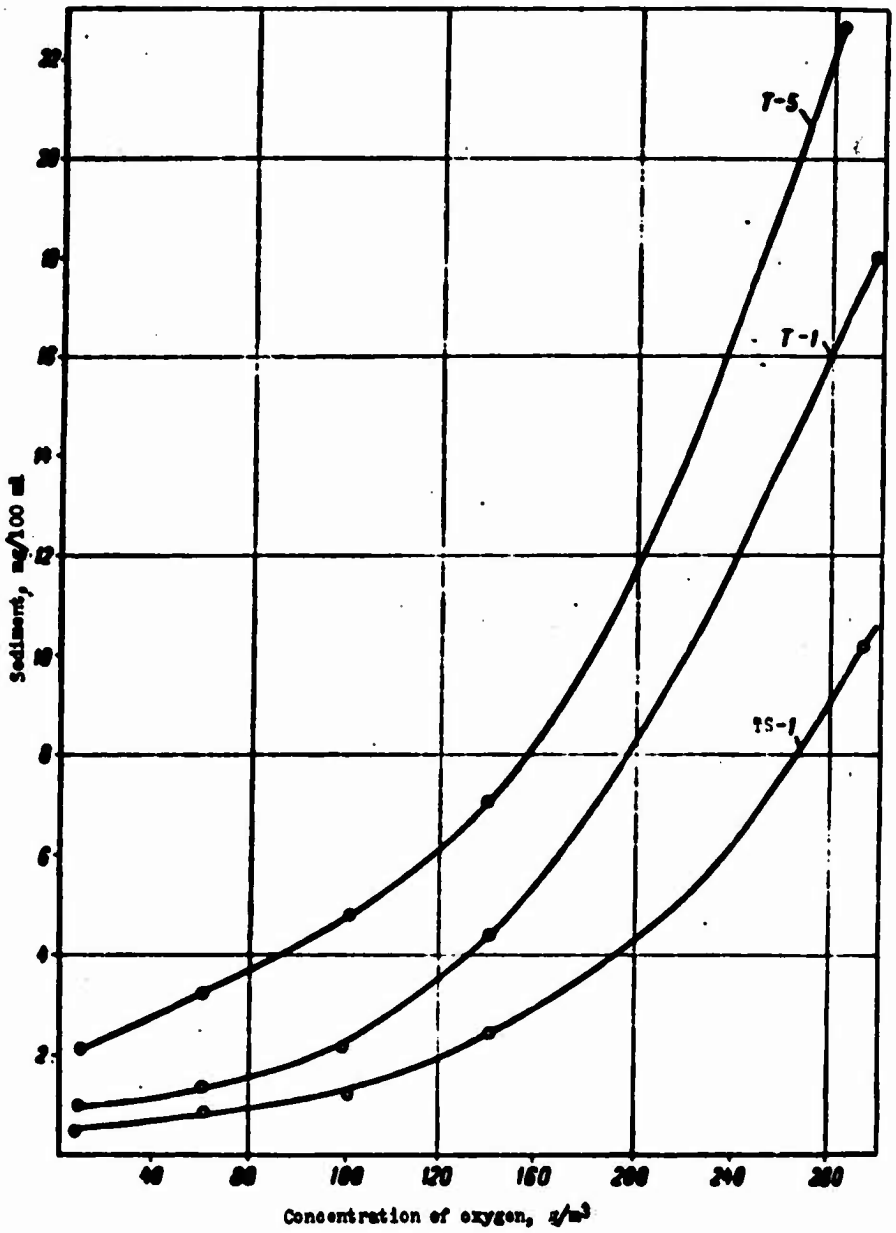

Fig. 49. Influence of concentration of oxygen in the gaseous medium on the formation of insoluble sediment at 150°C in contact with VB-24N bronze.

Influence of Metals

During its use in aircraft, fuel is in contact with various metals which are catalysts of reactions of oxidation of fuels at raised temperatures. An especially strong catalyzing action is rendered by copper and its alloys. Figure 50 shows the influence of metals – pure copper, BV-24 bronze, L-62 brass, duralumin D1T, and steel 12KhN3A – on sedimentation during heating of fuel TS-1 at 150°C for 6 hr.

Pure copper has the greatest influence on the formation of insoluble sediment. With an increase in the content in zinc alloys of copper the catalyzing effect of these alloys decreases. Copper and its alloys are also subject to the greatest corrosion.

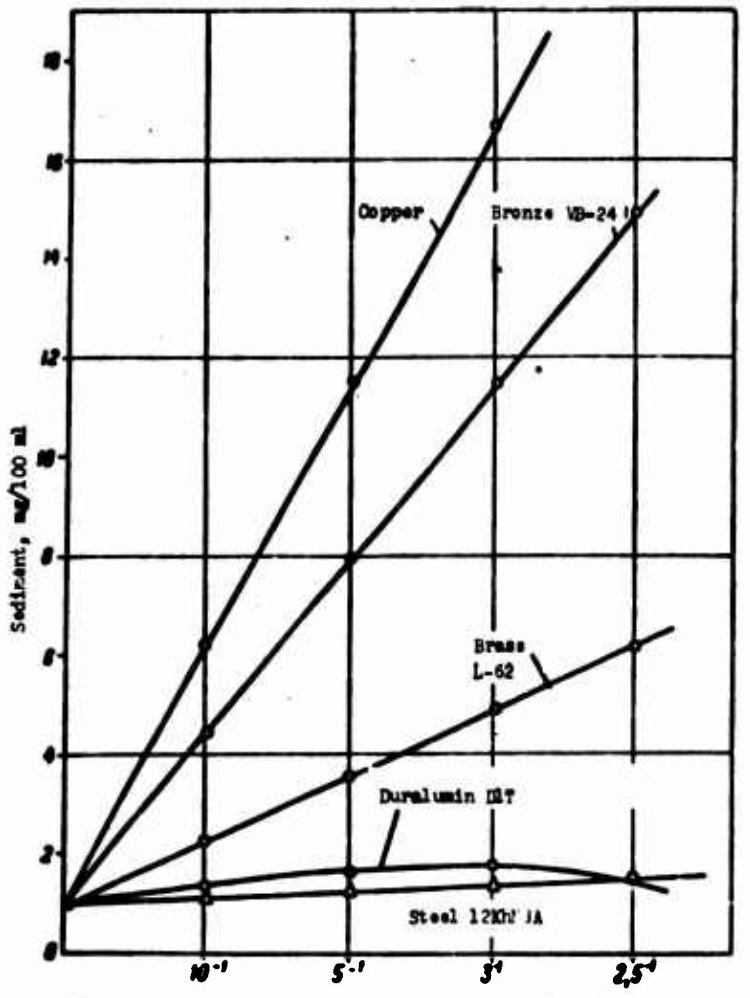

Fig. 50. Influence of metals on formation of sediment insoluble in fuel TS-1 at 150°C.

The minimum influence on stability of fuels is shown by steel 12KhN3A and duralumin D1T (Fig. 50). With an increase in the surface of metals in contact with heated fuels their catalyzing influence on the fuel increases.

Influence of Hydrocarbon Composition

Several studies have been made in which the influence of hydrocarbon composition on stability of propellants is considered [5, 9].

In these works the investigation of the influence of the hydrocarbon composition was conducted by an analogous method. After separation of heteroorganic compounds, the fuels were broken down into hydrocarbon groups: alkane-cyclane (AC), first aromatic (A_1), and second aromatic (A_2).

The A_2 fraction differed from the A_1 in increased cyclicity. Sulfur compounds were separated from aromatic fractions by two methods: oxidation of the fractions in an acetate medium by hydrogen peroxide, with subsequent separation of oxidation products from the hydrocarbons on silica gel; interaction with Rainey's nickel W-2 and subsequent filtering of the products of interaction from the hydrocarbon part.

During purification by hydrogen peroxide, besides sulfur compounds, hydrocarbons are separated; with Rainey's nickel unsaturated compounds were not removed. Thus thermooxidizing stability of fuels.

The thermooxidizing stability of parent fuels and of hydrocarbon groups at 150°C for 6 hr is shown in Table 48.

Table 48. Thermooxidizing Stability of Parent Fuels and Separated Hydrocarbon Groups

Designation of fuels and hydrocarbon groups	Sediment mg/100 ml	Tarry deposits on bronze g/m^2	Corrosion g/m^2	Optical density	Acidity, mg KOH/ 100 ml
Fuel TS-1					
Detarred fuel	4.0	0.2	0.2	0.037	1.2
Alkane-cyclane fraction	0	0	0	0	2.7
A_1 after removal of sulfur compounds on Rainey nickel	2.8	0.2	0.8	0.070	2.3
A_1 after removal of sulfur compounds by hydrogen peroxide ...	2.0	0.2	0.6	0.065	2.1
A_2 after removal of sulfur compounds on Rainey nickel	4.9	0.5	0.8	0.098	2.4
A_2 after removal of sulfur compounds by hydrogen peroxide ...	4.0	0.4	0.8	0.078	2.0
Fuel T-1					
Detarred fuel	5.8	0.2	0.4	0.047	3.0
Alkane-cyclane fraction	0	0	0	0	3.4
A_1 after removal of sulfur compounds on Rainey nickel	3.1	0.1	0.2	0.091	-
A_1 after removal of sulfur compounds by hydrogen peroxide ...	2.9	0.1	0.2	0.082	-
A_2 after removal of sulfur compounds on Rainey nickel	7.0	0.3	0.4	0.153	-
A_2 after removal of sulfur compounds by hydrogen peroxide ...	6.8	0.3	0.3	0.141	-
Fuel T-5					
Detarred fuel	7.2	0.4	0.8	0.088	4.0
Alkane-cyclane fraction	0	0	0	0.011	4.6
A_1 after removal of sulfur compounds on Rainey nickel	4.3	0.4	0.8	0.101	-
A_1 after removal of sulfur compounds by hydrogen peroxide ...	4.0	0.3	0.7	0.097	-
A_2 after removal of sulfur compounds on Rainey nickel	9.8	0.8	0.9	0.191	-
A_2 after removal of sulfur compounds by hydrogen peroxide ...	9.1	0.7	0.8	0.148	-

During heating of the alkane-cyclane hydrocarbons of fuel T-1, TS-1, and T-5 no insoluble sediment and deposits are formed; however, an increase in acidity in comparison with the parent fuels is observed, which attests to their intense oxidation without the formation of products of consolidation. Only with prolonged heating of the high-molecular alkane-cyclane hydrocarbons can sediment be formed [11].

During the heating of aromatic hydrocarbons there will be formed considerable quantities of insoluble sediment and gums and also carbonaceous acids. The corrosion fractions partially purified of sulfur by hydrogen peroxide and those purified by Rainey nickel, it is possible to establish that the presence of aromatic compounds with unsaturated side bonds leads to an increase in sediment and gum formation (Tables 48, 49). With an increase in the cyclicity of aromatic hydrocarbons, their thermooxidizing stability decreases. Since aromatic hydrocarbons form sediment and gum during heating and alkane-cyclane hydrocarbons do not, it is natural that with an increase in the content of aromatic hydrocarbons in fuels the quantity of gums and insoluble products of oxidation formed (Table 49). Aromatic hydrocarbons with raised cyclic recurrence (fraction A_2) have an especially intense negative influence on the stability fuels.

Tests of thermooxidizing stability of mixtures of alkane-cyclane hydrocarbons of fuels TS-1 and T-1 with α-methynapthalene (Table 50) confirm the conclusion that aromatic hydrocarbons, especially bicyclic, promote the appearance of sediment during heating of fuels. Apparently the smaller cyclic recurrence of aromatic hydrocarbons should explain the lower sediment formation during the heating of fuel TS-1 as compared to fuels T-1 and T-5, in spite of the large content of sulfur compounds in fuel TS-1.

An increase in molecular weight and, together with it, in cyclicity of molecules leads to an increase in the quantity of sediment formed during heating in both alkane-cyclane and aromatic hydrocarbons. Therefore a fuel of heavy fractional composition, containing more high-molecular compounds, will possess poorer thermal stability than a fuel of light fractional composition, even with an identical relationship of the various hydrocarbon groups.

Table 49. Influence of Content of Aromatic Hydrocarbons on Thermooxidizing Stability of Fuels

Aromatic hydrocarbons added to alkane-cyclane hydrocarbons of appropriate fuels	Sediment, mg/100 ml			Optical density		
	Content of aromatic fraction, wt %					
	5	10	15	5	10	15
A_1 fuel TS-1	0.2	0.6	1.4	0.005	0.014	0.020
The same after removal of sulfur compounds by hydrogen peroxide	0	0.4	0.8	0.002	0.006	0.009
A_1 fuel TS-1 after removal of sulfur compounds by Rainey nickel	0	0.4	1.0	0.004	0.012	0.020
A_2 fuel T-1	5.6	8.2	8.0	0.062	0.106	0.112
The same, after removal of sulfur compounds by hydrogen peroxide	0.8	1.0	1.4	0.014	0.017	0.021
The same, after removal of sulfur compounds by Rainey nickel	0.8	1.2	1.6	0.015	0.026	0.038

Table 50. Influence of α-Methylnapthalene on Thermooxidizing Stability of Alkane-Cyclane Fractions [ACF] of Fuels

Designation of mixtures	Sediment, mg/100 ml			
	Content of α-methylnapthalene, wt %			
	5	10	15	20
ACF of fuel TS-1 + α-methylnapthalene	0.2	0.6	0.8	1.4
ACF of fuel T-5 + α-methylnapthalene	1.4	1.6	-	2.4

Influence of Sulfur Compounds

It has been established that hydrocarbons of contemporary jet fuels (with the exception of the unsaturated, the content of which in straight run fuels is small) have relatively high thermooxidizing stability. Only atomatic hydrocarbons form a small quantity of sediment during oxidation. At present it is considered that the thermooxidizing stability of jet fuels is determined primarily by the content of heteroorganic compounds (sulfur, nitrogen, oxygen compounds). This is explained by the fact that heteroorganic compounds are easily subjected to oxidation, with the formation of products of consolidation – sediment and gums.

Therefore the question of the study of the influence of heteroorganic compounds, especially of sulfur, on the thermooxidizing stability of jet fuels becomes extremely urgent. Knowledge of the connection between the quantitative and qualitative composition of heteroorganic compounds and the thermooxidizing stability of fuels will allow more correctly and reliably to produce appraisals of raw materials and methods of purification, to select effective additives, and thereby considerably to increase reserves of high-quality fuels for supersonic aircraft.

Elemental sulfur. Elemental sulfur is found in jet fuels within limits of ten-thousandths of a percent. In these concentrations elemental sulfur has little effect on the stability and corrosion properties of jet fuels. However, with an increase in the content of elemental sulfur the properties of fuels deteriorate (Table 51).

Table 51. Influence of Elemental Sulfur on the Formation of Gums and on the Corrosivity of Fuels During Heating for 6 hr at 120°C [1, 2]

Designation of fuels to which elemental sulfur was added	Content of elemental sulfur		
	0	$1 \cdot 10^{-3}$	$4 \cdot 10^{-3}$
Fuel T-1:			
corrosion of bronze, g/m^2...	0.1	1.0	3.2
deposit on bronze, g/m^2.....	0.2	1.1	3.6
Fuel TS-1:			
corrosion of bronze, g/m^2...	0.1	1.0	7.0
deposit on bronze, g/m^2.....	0.2	1.2	8.0

Elemental sulfur essentially affects the oxidation of hydrocarbon fuels [1, 2]. In the oxidation of fuel in contact with bronze, with an increase in the content of elemental sulfur in the fuel the induction periods of oxidation were increased; however, the rate of oxidation was not essentially changed.

The increase in the induction period of oxidation of fuel should be related to the formation of a film of sulfurous copper on the surface of the metal, and, thus, a decrease of its catalytic effect. However, in operational conditions elemental sulfur can only cause harm, inasmuch as the film, consisting of oxides of copper and sulfurous copper, is nondurable and in certain conditions will be chipped, soiling the fuel and baring new layers of metal to enter into chemical reaction with

sulfur and oxygen. Corrosion of metal will be very intense and can lead to a change in the dimensions of components beyond the accepted allowances. Such a phenomenon presents a serious danger for the operating engine.

Mercaptans are very reactive compounds. For instance, it is well-known that in conditions of ordinary storage of fuel there occurs a decrease in the content of aromatic mercaptans because of their oxidation by atmospheric oxygen [2, 4, 6-8]. The negative role of mercaptans increases sharply with an increase in temperature. With an increase in the content of mercaptans the thermooxidizing stability of the fuel decreases (Table 52) and corrosion of metals which are in contact with heated fuel increases (Fig. 51).

Table 52. Influence of Mercaptans on Thermooxidizing Stability of Hydrogenated Fuel TS-1 (Without Contact with Metals) at 150°C for 6 hr [5, 6]

Indices	Content of mercaptan sulfur, %					
	0	0.005	0.007	0.010	0.020	0.03
Secondary octylmercaptan						
Weight of sediment, mg/100 ml	Absent	0.5	Not determined	0.6	0.8	1.0
Optical density	0	0.007	The same	0.011	0.015	0.040
Thiophenol						
Weight of sediment, mg/100 ml	Absent	1.8	3.2	4.7	6.5	10.8
Optical density	0	0.148	0.153	0.163	0.187	0.190

In experimental conditions no sediment was formed in hydrogenated fuel TS-1 without additions of mercaptans. The fuel remained transparent and colorless (Table 52). A small amount of sediment was formed in this hydrogenated fuel without mercaptans in contact with VB-24 bronze with heating (Fig. 51). With the presence in the fuel of mercaptans there occurs formation of insoluble sediment, which increases with an increase in the content of mercaptans. The quantity of sediment formed depends on the structure of the mercaptans and on the conditions of the contact of heated fuel with metals – in particular, with bronze. With heating of fuels containing aromatic mercaptans but not in contact with metals, there will be formed more sediment than during the heating of fuels with admixtures of aliphatic mercaptans.

Conversely, in the presence of copper alloys, heated jet fuel with admixtures of aromatic mercaptans will form less sediment than fuel with admixtures of aliphatic mercaptans.

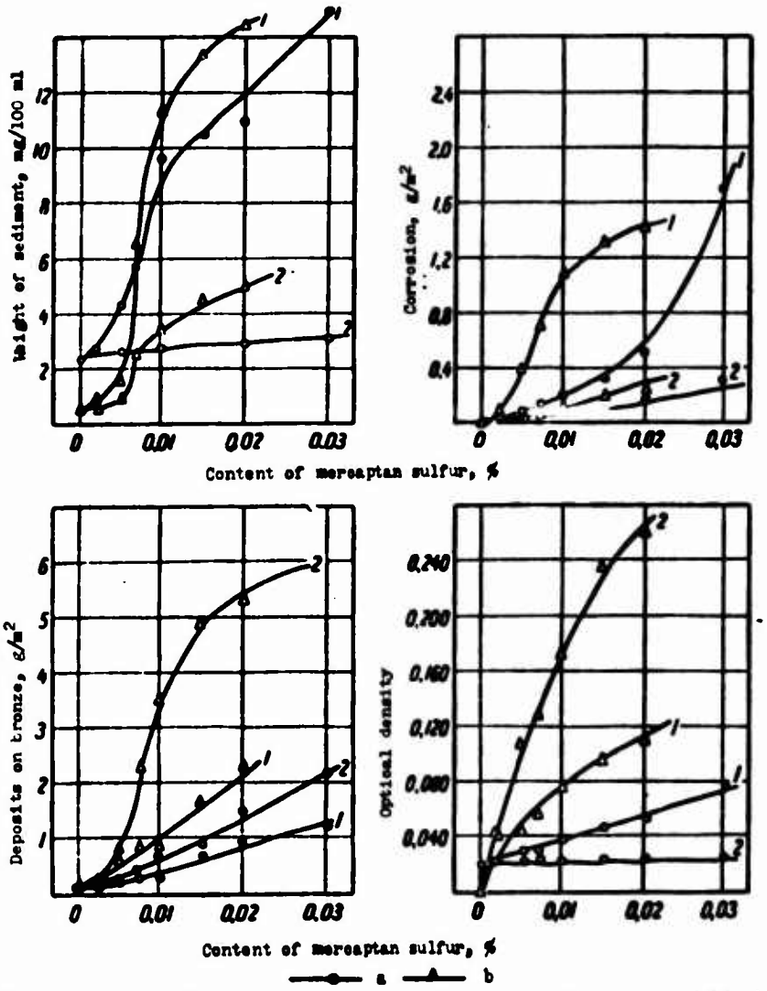

Fig. 51. Influence of mercaptans on thermooxidizing stability and corrosivity of fuel TS-1 at 150°. 1 – hydrogenated fuel TS-1 + secondary octylmercaptan; 2 – hydrogenated fuel TS-1 + thiophenol; a) in brass vessels; b) in glass vessels.

This is explained by the fact that aromatic mercaptans oxidize rapidly and form a protective tarry film on the surface of the metal [5].

The negative influence of mercaptans varies with temperature and concentration (Fig. 52). At a temperature of 100°C the presence of mercaptans in fuel in quantities up to 0.005% has practically no effect on the increase of sedimentation. A noticeable increase in the formation of sediment is observed with concentrations of mercaptan sulfur of 0.007% and subsequently sedimentation increases with an increase in the content of mercaptan sulfur in the fuel. At temperatures from 150 to 300°C, with addition of aliphatic mercaptans to fuel there is observed a sharp increase in sedimentation; this is the most considerable with the addition of the first portions of the mercaptan sulfur (up to 0.01%). With a content of mercaptan sulfur of 0.01%, 3-5 times more sediment was formed than in the parent fuel TS-1.

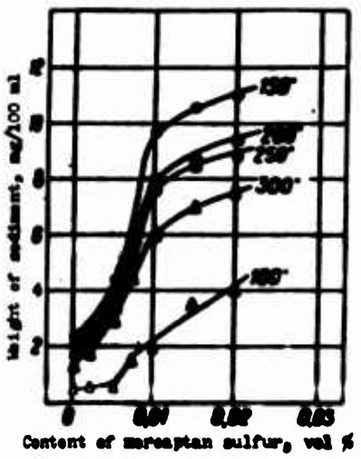

Fig. 52. Influence of secondary octylmercaptans on sedimentation in hydrogenated fuel TS-1 at various temperatures.

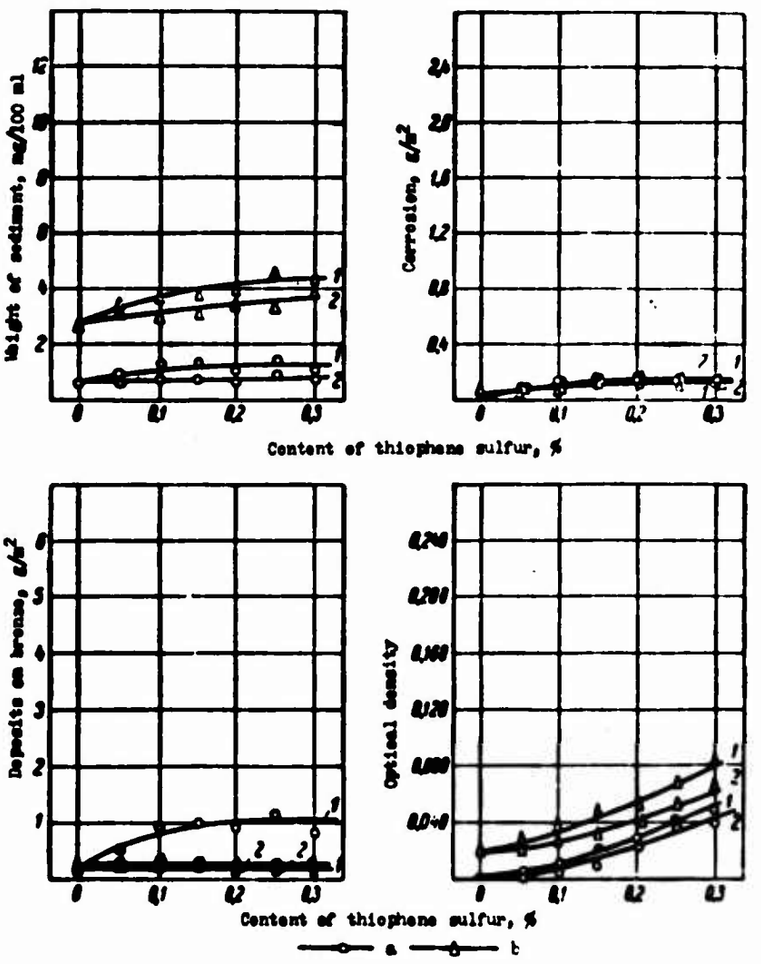

Fig. 53. Influence of thiophenes on thermooxidizing stability of fuel TS-1 at 150°C. 1 — hydrogenated fuel TS-1 + α-octylthiophene; 2 — hydrogenated fuel TS-1 + thiophene, a) in glass vessels; b) in brass vessels.

Thus a noticeable negative action of mercaptans at a temperature of 100°C appears starting from a concentration of 0.007%; at temperatures of 150-300°C it appears from a concentration of 0.001-0.002%. With an increase in temperature there occurs consolidation and coagulation of particles of sediment insoluble in the fuel.

Thiophenes. Thiophenes insignificantly worsen the thermooxidizing stability and increase the corrosivity of fuels with heating to 200°C (Fig. 53).

A somewhat greater negative influence on thermooxidizing stability is rendered by α-octylthiophene. The introduction of the side chain, obviously, increases the reactivity of thiophenes.

A maximum in the quantity of sediment formed is observed at 150°C (Fig. 54). With an increase in the concentration of α-octylthiophene in fuel TS-1 to 0.3%, sedimentation was increased by less than two times.

In standard fuels homologues of thiophene exist in quantities of 0.05-0.08% and less in conversion to sulfur. The presence of such quantities of thiophenes, obviously, will have no essential negative effect on the stability and corrosion properties of jet fuels with heating to 200°C.

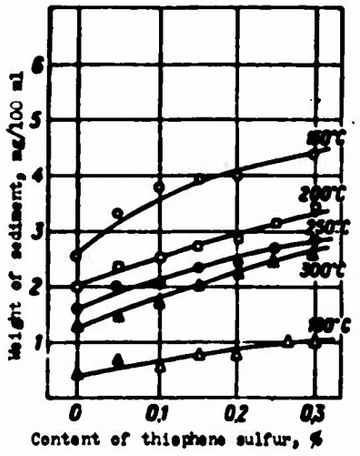

Fig. 54. Influence of α-octylthiophene on sedimentation in hydrogenated fuel TS-1 at various temperatures.

Thiophanes. Thiophanes, as a rule, impair the thermooxidizing stability of fuel to a greater degree than thiophenes (Fig. 55). In the presence of thiophanes there is observed an increase in the amount of sediment and gums; the corrosivity of fuels also increases.

The negative influence of thiophanes is in many respects, determined by the structure and length of side chains. When there is an aliphatic side chain the thermooxidizing stability of the fuel is impaired [only] insignificantly. A noticeable impairment of thermooxidizing stability is observed in the presence of α-(3-phenylpropl)- thiophene. Thiophanes with branched aliphatic and side chains occupy an intermediate position.

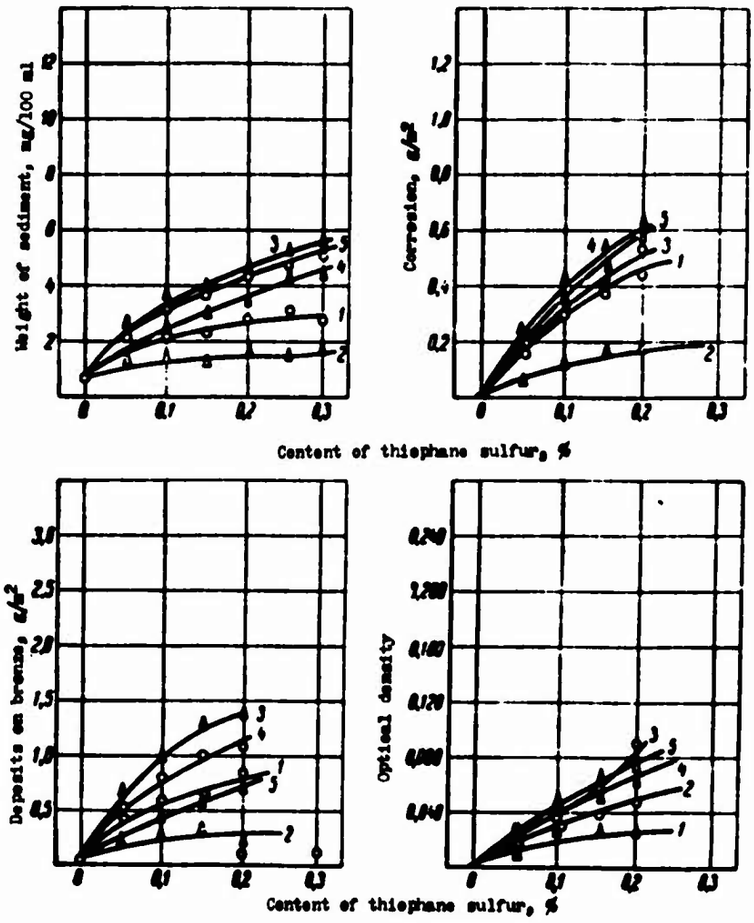

Fig. 55. Influence of thiophanes on thermooxidizing stability of fuel TS-1 at 150°C. 1 — hydrogenated fuel TS-1 + α-hexylthiophane; 2 — hydrogenated fuel TS-1 + α-octylthiophane; 3 — hydrogenated fuel TS-1 + + α-(3-phenlpropl)- thiophane; 4 — hydrogenated fuel TS-1 + α-(2-methylbutyl)-thiophane; 5 — hydrogenated fuel TS-1 + α-(2-methylamyl)-thiophane.

Sulfides. Sulfides render a significant negative influence on fuel; the influence of the sulfides, other things being equal, is entirely determined by the structure of the hydrocarbon radical (Fig. 56). In the presence of aromatic sulfides, during heating of the fuel there is observed stronger corrosion of bronze and the amount of sediment and gums is increased; aliphatic sulfides impair the thermo-oxidizing stability of fuel to a smaller degree.

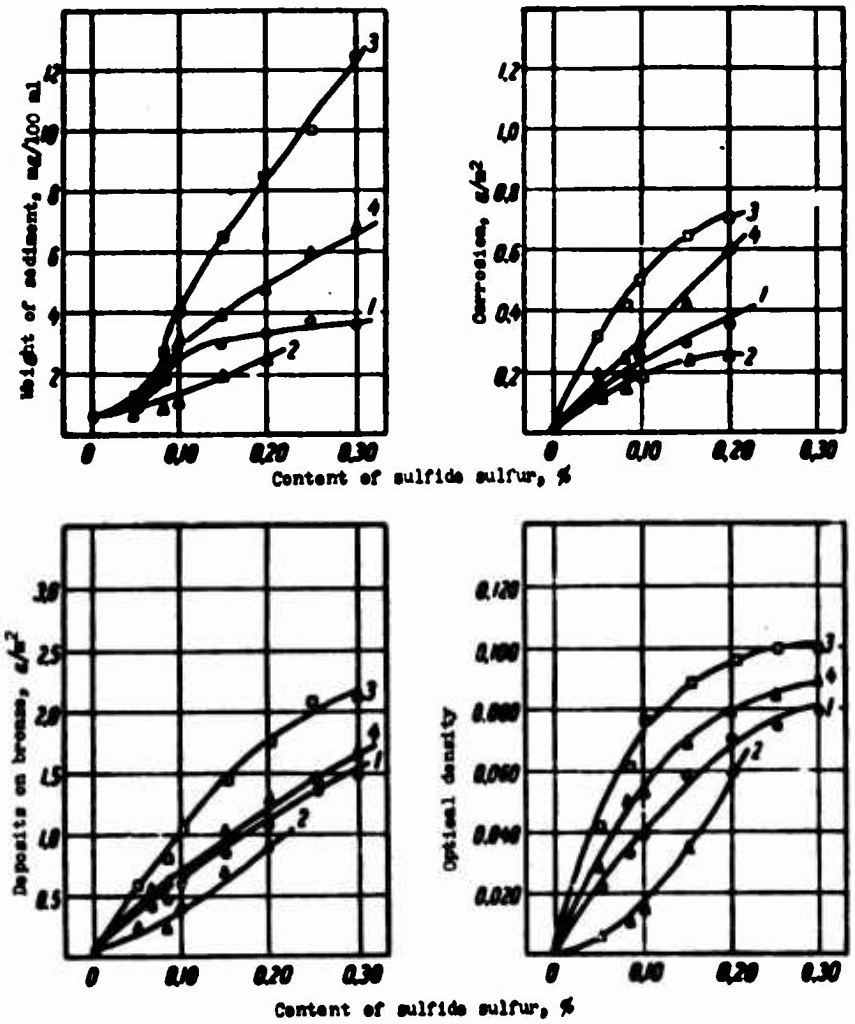

Fig. 56. Influence of sulfides on thermooxidizing stability of fuel TS-1 at 150°C (in glass vessels). 1 – hydrogenated fuel TS-1 + butyl-sec-octyl sulfide; 2 – hydrogenated fuel TS-1 + diiso-sec-heptyl sulfide; 3 – hydrogenated fuel TS-1 + isohexylphenyl sulfide; 4 – hydrogenated fuel TS-1 + methylbenzyl sulfide.

More soluble gums will be formed in the presence of aromatic sulfides than in the presence of aliphatic sulfides (Fig. 56). Figure 57 gives data characterizing the influence of temperature and sulfide concentration on the formation of sediments insoluble in fuels. As can be seen from the figure, in the presence of diiso-sec-heptyl sulfide at 100°C there is observed only an insignificant increase in sedimentation. Noticeably increased sedimentation occurs at 150°C and above and a

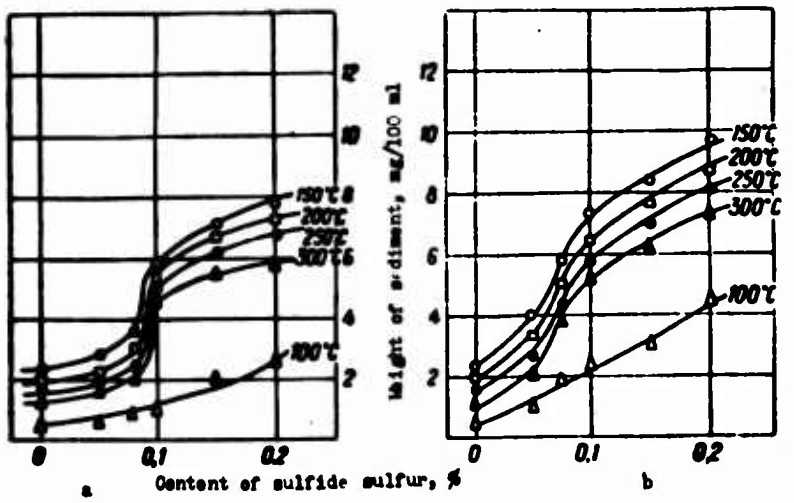

Fig. 57. Influence of diiso-sec-heptyl sulfide (a) and isohexylphenyl sulfide (b) on sedimentation in hydrogenated fuel TS-1 at various temperatures.

concentration of 0.08% in conversion to sulfur. In the presence of aromatic sulfides the increase in the quantity of sediment formed occurs more intensely in the entire temperature range.

Influence of disulfides.

Disulfides impair the thermooxidizing stability of fuel more strongly than sulfides and thiophanes (Fig. 58). The optical density of the fuel during heating changes strongly at concentrations of disulfides up to 0.1%; subsequently the curve of optical density becomes more shallow. With an increase in the content of disulfides the formation of sediment grows intensely. The corrosion of bronze and the formation of deposits on it are also increased with an increase in the concentration of disulfides.

Figure 59 shows the influence of temperature and the concentration of disulfides on the thermooxidizing stability of hydrogenated fuel TS-1. At a temperature of 150°C and above at concentrations of disulfide sulfur in the fuel of 0.02% there is observed a sharp increase in sedimentation; this increase is stronger with addition of di-sec-octyl disulfide than with diphenyl disulfide.

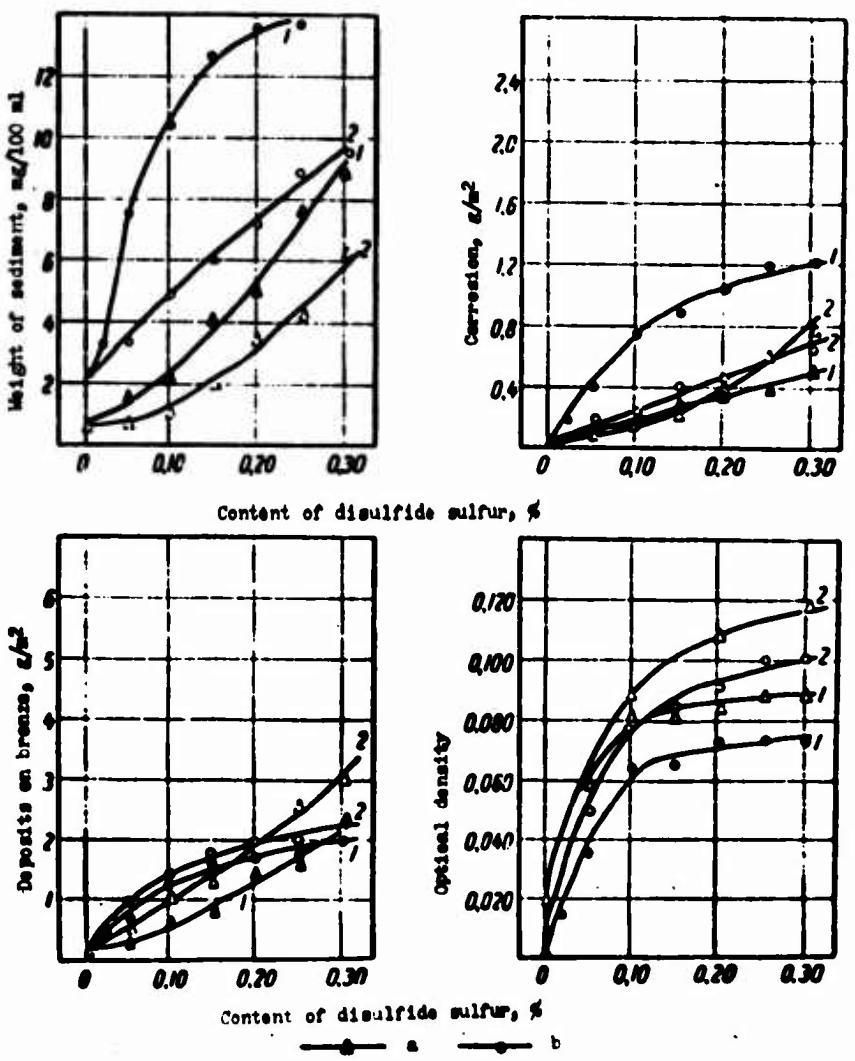

Fig. 58. Influence of disulfides on thermooxidizing stability of fuel TS-1 at 150°C. 1 – hydrogenated fuel TS-1 + di-sec-octyl disulfide; 2 – hydrogenated fuel TS-1 + diphenyl disulfide; a) in brass vessels; b) in glass vessels.

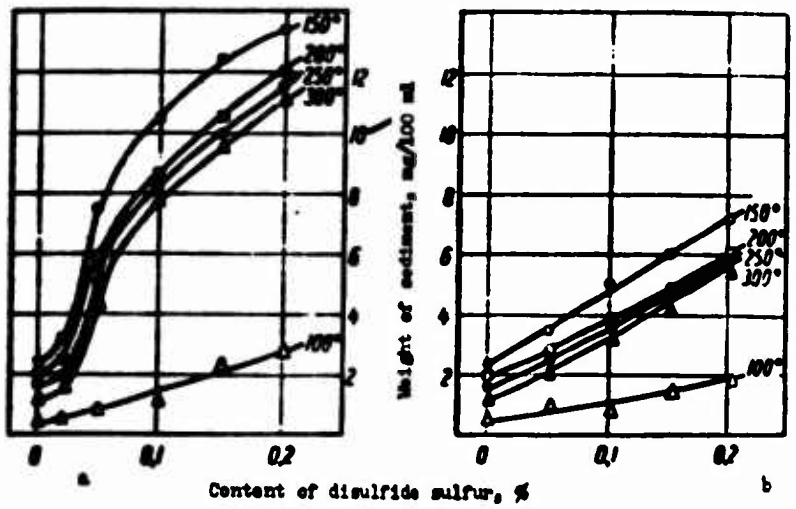

Fig. 59. Influence of disulfides on the information of sediment insoluble in fuels at various temperatures: a) hydrogenated fuel TS-1 + di-sec-octyl disulfide; b) hydrogenated fuel TS-1 + + diphenyl disulfide.

Influence of artificial mixtures of sulfur compounds. Table 53 gives data characterizing the influence of mixtures of sulfur compounds on the stability and corrosivity of hydrogenated fuel TS-1. These data are interesting in that they permit estimating the mutual influence of individual sulfur compounds during their simultaneous presence. The first mixture approximately corresponds to the group composition of sulfur compounds in commercial fuels. The corrosion effect on bronze of hydrogenated fuel with a mixture of sulfur compounds turned out to be almost the same as the effect of standard fuel TS-1.

At a temperature 100°C the presence of a mixture of sulfur compounds in a quantity of 0.255% (per GOST 10227-62 0.25% is allowed) whose composition includes up to 0.005% mercaptan and 0.02% disulfide sulfur leads to insignificant impairment of thermooxidizing stability. Sharp impairment of thermooxidizing stability occurs with heating to a temperature of 150°C. Successive removal of mercaptan and disulfide sulfur acts favorable on the thermooxidizing stability of fuel, although the latter remains quite low. For essential improvement of the thermooxidizing stability of fuels, it is necessary not only to remove mercaptan and disulfide sulfur but also to lower the total content of sulfide sulfur. Table 54 gives generalized data on the limiting content of sulfur compounds at temperatures of 100 and 150°C. Once the indicated concentrations of sulfur compounds are exceeded in fuels, there is observed an intense increase in corrosivity and a decrease in the stability of fuels.

Table 53. Influence of Mixtures of Individual Orgonosulfur Compounds on Thermooxidizing Stability of Hydrogenated Fuel TS-1 [5]

Addition of mixture of sulfur compounds	Concentration in conversion to sulfur wt %	Test temperature of fuel with mixture of sulfur compounds, °C	Sediment insoluble in fuel, mg/100 ml	Corrosion, g/m²	Optical density
Initial fuel TS-1	—	150	2.4	Absent	0.020
Mixture 1:					
secondary octylmercaptan	0.005	100	3.5	0.1	0.045
α-octylthiophene	0.10	150	17.5	0.8	0.183
diiso-sec-heptyl sulfide	0.08	200	15.1	0.7	0.167
isohexylphenyl sulfide	0.05	250	13.2	0.7	0.159
di-sec-octyl sulfide	0.02				
Total	0.255				
Mixture 2:					
α-octythiophene	0.10	100	3.2	0.1	0.037
diiso-sec-heptyl sulfide	0.08	150	14.8	0.6	0.73
isohexylphenyl sulfide	0.05	200	12.4	0.4	0.68
di-sec-octyl sulfide	0.02	250	11.1	0.3	0.49
Total	0.25				
Mixture 3:					
α-octylthiophene	0.10	100	2.9	Absent	0.029
diiso-sec-heptyl sulfide	0.08	150	9.3	0.5	0.169
isohexylphenyl sulfide	0.05	200	7.8	0.4	0.153
Total	0.23				

Table 54. Limiting Content of Sulfur Compounds, After Which Intense Impairment of Thermooxidizing Stability of Fuels Is Observed

Sulfur compounds	Temperature, °C	Permissible content of sulfur compounds, wt % (on sulfur)
Mercaptans	100	0,005
	150 and more	0,002
Thiophenes	100	0,20
	150	0,10
Aromatic sulfides	100	0,05
	150	0,05
Aliphatic sulfides	100	0,10
	150	0,08
Disulfides	100	0,05
	150	0,02

At present the question of the review of the permissible total content of sulfur compounds in fuels and also of the quantitative limitation of the content of sulfur compounds by groups has become very urgent.

Influence of Sulfur Compounds on Particle Size of Insoluble Sediment Formed During Heating

In the process of storage and application of fuels of different chemical composition there occurs formation and enlargement of solid particles insoluble in fuel [5, 12, 13]. The process of formation of sediment insoluble in fuels is intensified with an increase in the temperature of the fuel [14]. Enlargement of particles of insoluble sediment occurs mainly because of aggregation of small particles into larger ones [14, 15].

The increase in the requirements for thermooxidizing stability of contemporary jet fuels leads to the necessity of determining the quantity of insoluble sediment or the time of clogging of filtering elements in the fuel system. The determination of the quantity of insoluble sediment formed in the fuel does not completely exhaust the problem if there is not a sufficiently clear presentation about the coarseness of its particles. Actually, there can be a fuel with a considerable content of insoluble sediment, but with particles with dimensions up to 2 μ. Such a fuel will pass through the filtering, pumping, and distributing system of the engine and will burn, probably, without special complications. However, there can be another case when the quantity of sediment is small but its particles have dimensions exceeding those of the mesh of the filtering elements of the fuel system. In this case the filters will be intensely obstructed by sediment, the pressure drop on the filters will increase, and fuel feed into the combustion chamber will progressively decrease. Consequently, along with the total amount of sediment, its particle size has great significance.

Recently it has been established that sulfur compounds have a large influence both on the formation and on the enlargement of sediment insoluble in fuel [5, 14, 16]. To determine particle size of insoluble sediment formed in fuel the method of screen analysis is most often used [6, 14].

With heating of hydrogenated fuel TS-1 with an insignificant content of sulfur compounds, comparatively little insoluble sediment will be formed; here 80% of the sediment has dimensions of particles less than 5-7 μ (Fig. 60). Thus almost all the sediment formed in hydrogenated fuel after its prolonged heating at 150°C will pass freely through engine filtering elements with mesh dimensions of 15-20 μ.

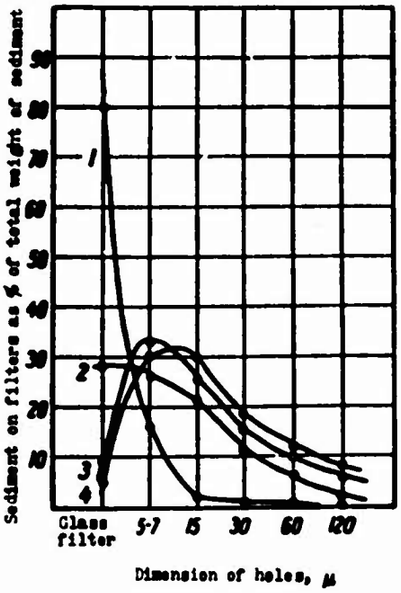

Fig. 60. Screen composition of sediment formed in fuel TS-1 with heating. 1 — hydrogenated fuel TS-1; 2 — fuel TS-1 with total sulfur 0.146%; 3 — fuel TS-1 with total sulfur 0.136%; 4 — fuel TS-1 with total sulfur 0.156%.

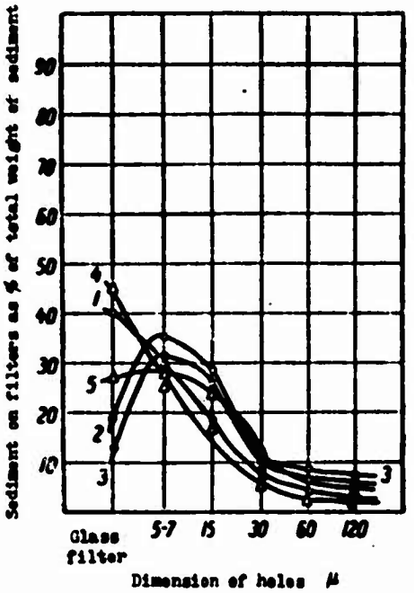

Fig. 61. Influence of mercaptans on size of particles insoluble in fuel. 1 — hydrogenated fuel TS-1 + 0.005% secondary octylmercaptan; 2 — the same, + 0.0109 [%] secondary octylmercaptan; 3 — the same, + 0.020% secondary octylmercaptan; 4 — the same, + 0.005% thiophenol; 5 — the same, + 0.010% thiophenol.

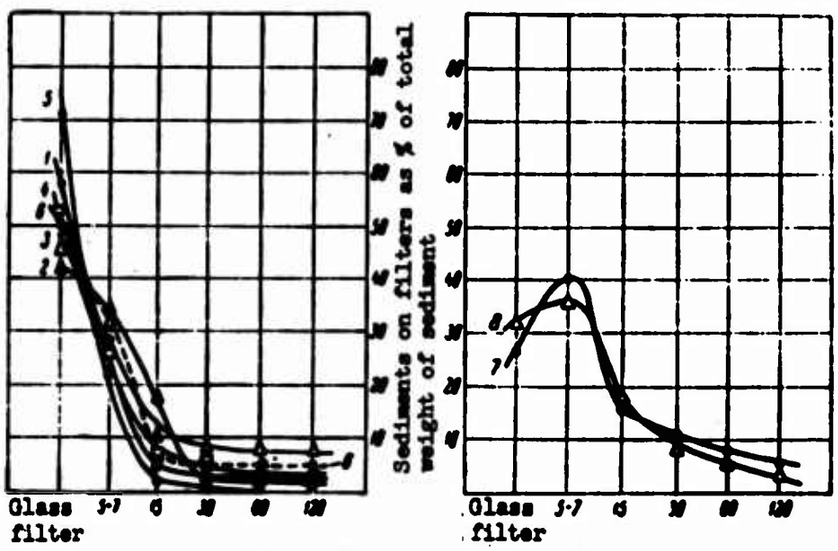

Fig. 62. Influence of various sulfur compounds on particle size of sediment insoluble in fuels. Hydrogenated fuel TS-1 with addition 0.1% (in conversion to sulfur) of: 1 — α-(3-phenylpropyl)- thiophane; 2 — isohexyl phenyl sulfide; 3 — butyl-sec-octyl sulfide; 4 — α-(2-methylpropyl)-thiophane; 5 — α-octylthiophane; 6 — sulfur compounds separated from aromatic fractions of fuel TS-1; 7 — di-sec-octyl sulfide; 8 — diphenyl disulfide.

The presence of sulfur compounds in unpurified standard fuels TS-1 leads to an increase in the quantity and coarseness of formed sediment (Fig. 60). Of all the sulfur compounds, the mercaptans have the strongest effect on enlargement of the insoluble particles of sediment formed (Fig. 61).

Other sulfur compounds have less effect on the enlargement of sediment particles (Fig. 62). In terms of their ability to enlarge particles of sediment, sulfur compounds are disposed in the following ascending series: thiophenes → thiophanes → → sulfides → disulfides → mercaptans.

With an increase in the concentration of sulfur compounds (independently of their structure) the coarseness of formed sediment particles is increased.

Influence of Nitrogen Compounds

Nitrogen compounds exist in jet fuels in small quantities, within the limits 0.07-0.1%. In work carried out by the authors on the study of the influence of natural nitrogen compounds on the thermooxidizing stability of fuels [18], nitrogen bases were separated from fractions of tarry substances of fuels. The characteristics of separated nitrogen concentrates is given in Table 55. With addition of the separated nitrogen concentrates to fuels, it was found that in certain limits of content of nitrogen concentrates the thermooxidizing stability of fuels increases and then drops (Fig. 63).

For fuel TS-1 and T-1 these concentrations constitute about 0.05%. Such a positive influence of nitrogen concentrates on the thermooxidizing stability of fuels is explained by the presence among them of compounds of the type of quinoline and xylidine and also heterocyclic compounds, which are characterized by the presence in the ring of nitrogen atoms and functional groups – thiol, amine, hydroxyl [5, 18, 19].

Influence of Tarry Substances

Z. A. Sablina and A. A. Gureyev [17] separated tarry substances from fuels by chromatographic means on activated aluminum oxide. The separated tarry substances were then added to the parent fuel invarious concentrations, after which these mixtures were tested on a pumping installation at high temperatures. The authors established that with an increase in the content of tarry substances the stability of fuels sharply deteriorates; this is expressed in an intense increase in sedimentation.

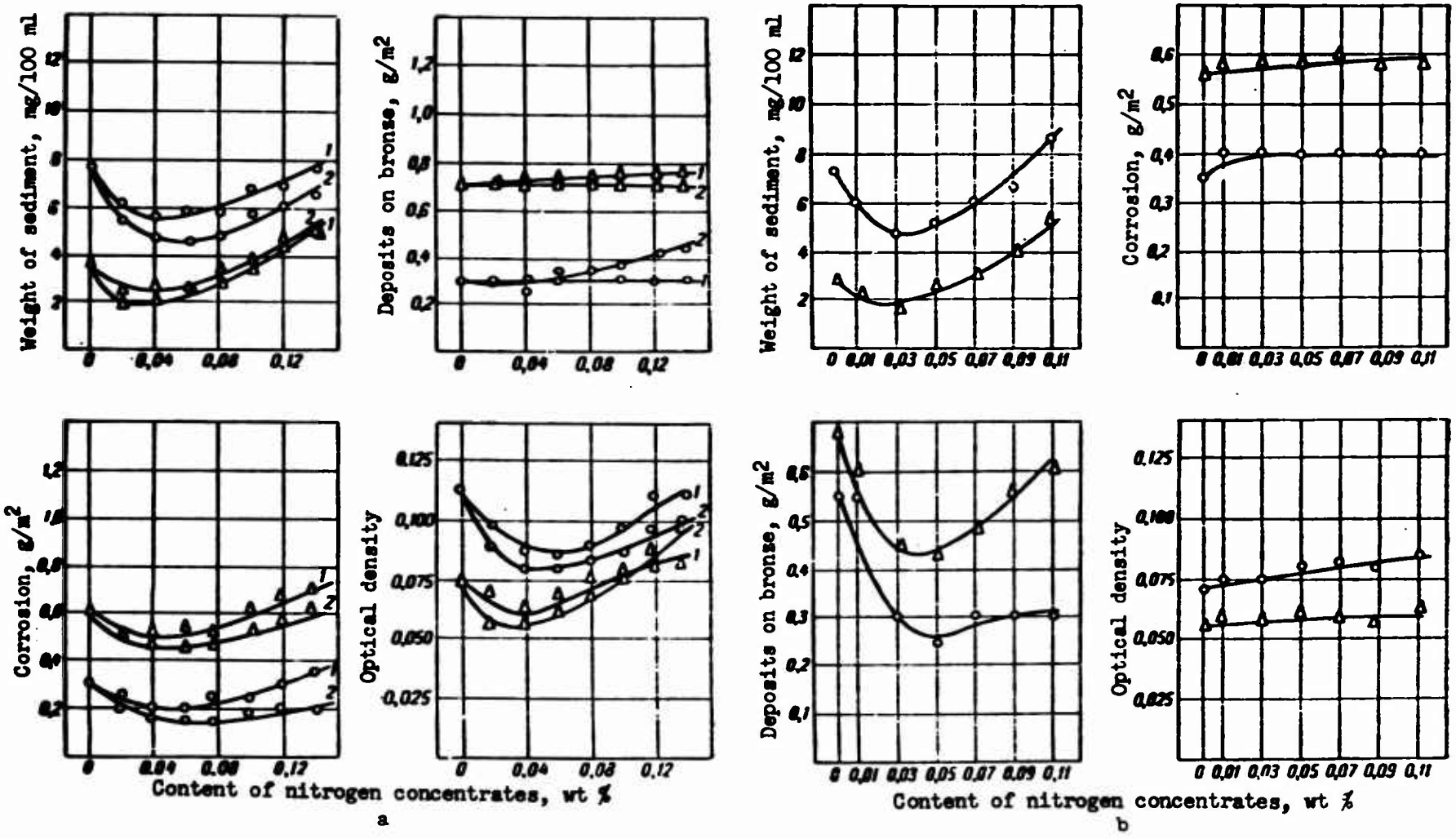

Fig. 63. Influence of nitrogen bases on the thermooxidizing stability of jet fuels T-1 (a) and TS-1 (b). 1 — benzene fraction; 2 — alcohol-acetone fraction. Circles designate test in brass vessels; triangles, in glass vessels.

Table 55. Physicochemical Properties of Nitrogen Concentrates Separated from Fractions of Tars of Fuels

Indices	Nitrogen compounds separated from the alcohol-acetone fraction of tars of fuel TS-1	Fuel T-1		Fuel DA	
		Nitrogen compounds separated from the benzene fraction of tars	Nitrogen compounds separated from alcohol-acetone fraction of tars	Nitrogen compounds separated from the benzene fraction of tars	Nitrogen compounds separated from the alcohol-acetone fraction of tars
Molecular weight	193.5	210,11	232,4	243,1	302,4
Refractive index n_D^{20}	1,5241	1,5248	1,5305	1,5289	1,5383
Density ρ_4^{20}	1,0039	1,0112	1,0835	1,0139	1,1010
Iodine number g/100 g ..	31,4	40,1	38,4	36,7	48,3
Experimental composition, %:					
C	79,98	82,32	73,71	72,41	72,17
H	10,13	9,36	8,92	9,82	10,01
S	2,32	1,54	1,80	1,25	4,12
N	5,86	5,67	11,63	8,81	6,81
O (by difference)	1,91	1,11	3,94	7,71	6,89
Empirical formula	$C_{14,3}H_{19,6}S_{0,14}N_{0,78}O_{0,22}$	$C_{14,5}H_{19,7}S_{0,1}N_{0,85}O_{0,15}$	$C_{12,9}H_{20,6}S_{0,13}N_{1,93}O_{0,57}$	$C_{14,6}H_{23,8}S_{0,1}N_{1,52}O_{1,17}$	$C_{18,1}H_{30,8}S_{0,39}N_{1,47}O_{1,3}$

Ya. B. Chertkov and V. N. Zrelov also established [9] that thermooxidizing stability worsens with an increase in the content in fuel of tarry substances separated on silica gel (Table 56).

Table 56. Influence of Tarry Substances on Thermooxidizing Stability of Fuel T-1 [9]

Fuels	Concentration of tarry substances, mg/100 ml	Sediment, mg/100 ml	Deposits on bronze, g/m²	Corrosion, g/m²
Parent fuel.....	Not determined	12.5	0.4	0.5
Detarred fuel.....	0	1.9	0.2	0.2
The same	25	4.5	0.2	0.3
The same	50	6.4	0.3	0.4
The same	75	8.0	0.3	0.4
The same	100	9.6	0.3	0.4
The same	125	10.2	0.6	0.4
The same	150	10.4	0.6	0.6
The same	175	10.6	0.7	0.9

From the given data one can see that after the removal from fuel T-1 of the main part of the tars sedimentation decreased by approximately 6 times. Corrosion and formation of gummy deposits on bronze also decrease. With an increase in the content in the fuel of tons, sedimentation, deposits, and corrosion of bronze increase and gradually attain the magnitudes characteristic for the unpurified present fuel.

P. I. Davydov and G. F. Bol'shakov established that natural tarry substances contained in jet fuels can, in optimum concentrations, increase their stability and anticorrosive properties [7]. Figures 64 and 65 show data on the influence of tarry substances separated from fuel TS-1 by chromatographic means with benzene and a mixture of alcohol and acetone. At tar concentrations of 0.12-0.13% there was observed a decrease in sedimentation in fuels (Fig. 64); at concentrations of 0.08-0.09% the corrosion of bronze and the formation on it of gummy deposits were minimal (Fig. 65). An analogous regularity was observed during

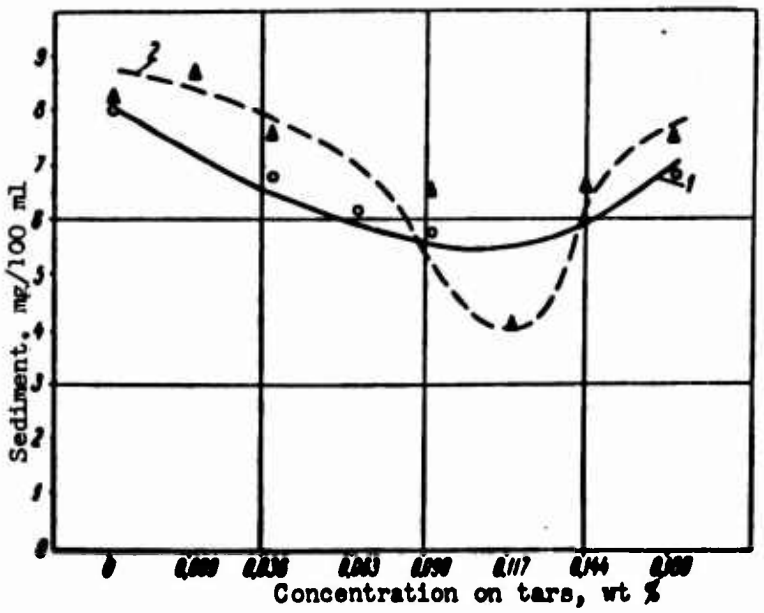

Fig. 64. Influence of tarry fractions on formation of insoluble sediment in fuel TS-1. 1 – benzene fraction; 2 – alcohol-acetone fraction.

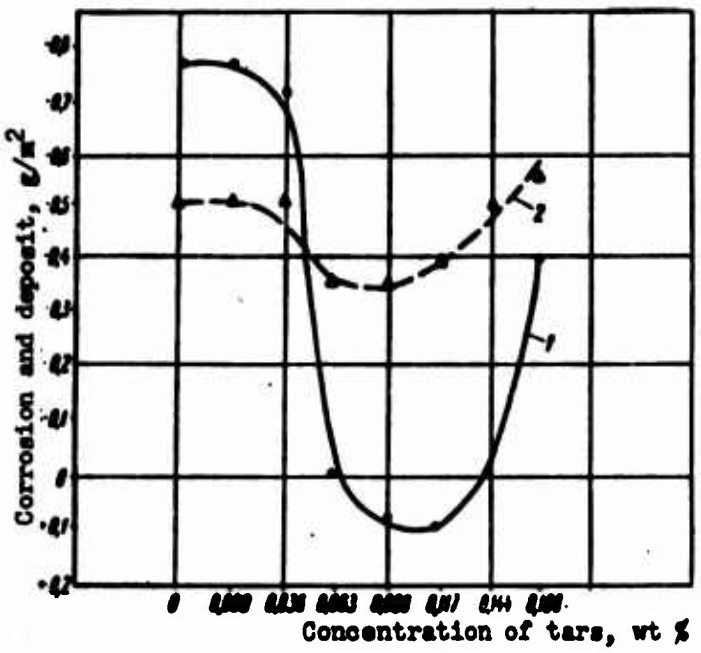

Fig. 65. Influence of benzene fraction of tars on the formation of gummy deposits on metal and on the corrosivity of fuel TS-1. 1 — corrosion, 2 — deposit.

tests of mixtures of detarred fuel T-5 with tars separated from it by silica gel; only the optimum content was different (Fig. 66). It has been shown that the increase in stability and the decrease of corrosion aggressiveness of jet fuels in the presence of natural tars is connected primarily with the presence in the tars of certain sulfur- and nitrogen-containing compounds [5, 7, 18, 19].

During storage tars are accumulated in jet fuels; the character of these tars differs essentially from that of initial tars (Table 57).

Tars formed during storage of detarred fuel are characterized by large iodine and acid numbers and somewhat raised values of density, refractive index, and molecular weight; they contain less sulfur and nitrogen and considerably more oxygen as compared to tars separated from the parent fuel.

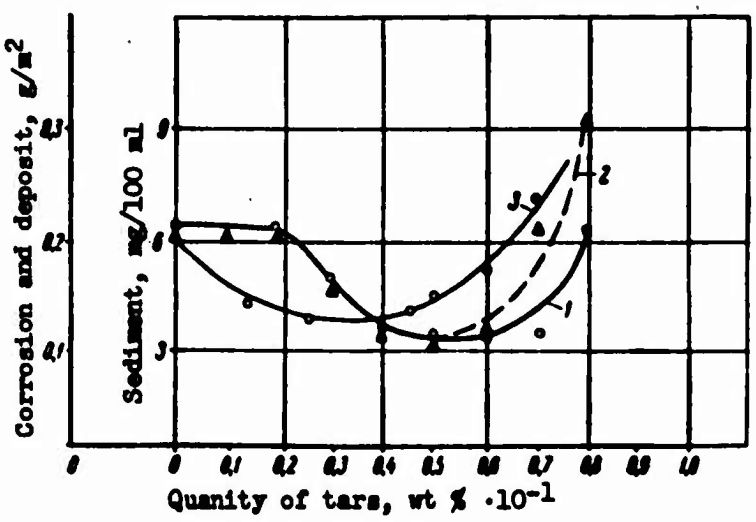

Fig. 66. Influence of tarry substances on stability and corrosivity of fuel T-5. 1 — corrosion; 2 — deposit; 3 — sediment.

After a year's storage of twice-detarred fuel TS-1 tars were separated from it anew. These tars were characterized by still greater acidity and by a larger content of unsaturates and values of molecular weight, density, and refractive index. In these tars there was still more oxygen and less sulfur and nitrogen.

Table 57. Characteristics of Tarry Substances Separated from Fuel TS-1

Indices	Tars of parent fuel TS-1	Tars formeducated in detarred TS-1 during storage for one year	Tars formed in twice-detarred fuel TS-1 after storage for one year
Density ρ_4^{20}	0.9573	0.9671	0.9689
Refractive n_D^{20}	1.4957	1.5137	1.5184
Molecular weight	185.4	192.3	198.4
Iodine number g iodine/100 g fuel	32.4	90.8	110.4
Acid number, mg KOH/100 ml	2.61	20.45	40.4
Surface tension, dyne/cm	27.9	29.3	30.1
Elemental composition %:			
C	78.04	76.31	77.57
H	9.18	9.02	8.91
S	7.54	4.38	1.21
N	0.35	0.08	0.04
O (by difference) ..	4.89	10.21	12.27
Yield, wt %	0.045	0.183	0.384

The presence in the tars formed during storage of preliminarily detarred fuels of sulfur, nitrogen and oxygen indicates that in fuels earlier liberated from tars, including tars inhibiting oxidation of compounds, processes of oxidation are intensely developed; here oxidation is undergone primarily by low-stability components: the remaining part of the heteroorganic compounds and unsaturated hydrocarbons.

In terms of effect on the thermooxidizing stability of fuel TS-1, the three fractions of tarry substances are very different from each other (Fig. 67). With their addition to detarred fuel, tars formed during storage considerably increased sedimentation during heating. Sedimentation in fuel is increased with an increase in the concentration of tars, whereas the curve of formation of insoluble sediment in the presence of tars separated from freshly obtained fuel has a minimum at concentrations of 0.04-0.07 wt. %. The corrosivity of fuels in the presence of these and other tars at contents up to 0.07 wt. % is practically identical. With a further increase in the quantity of tars, the acid tars formed during storage of the fuel corrode bronze VB-24 more intensely as compared to tars separated from parent fuel TS-1.

Thus, with heating of fuels in the presence of acid tars formed during storage of fuels, the processes of corrosion of bronze and formation of insoluble gums and sediment flow more intensely than in fuels with primarily separated tars.

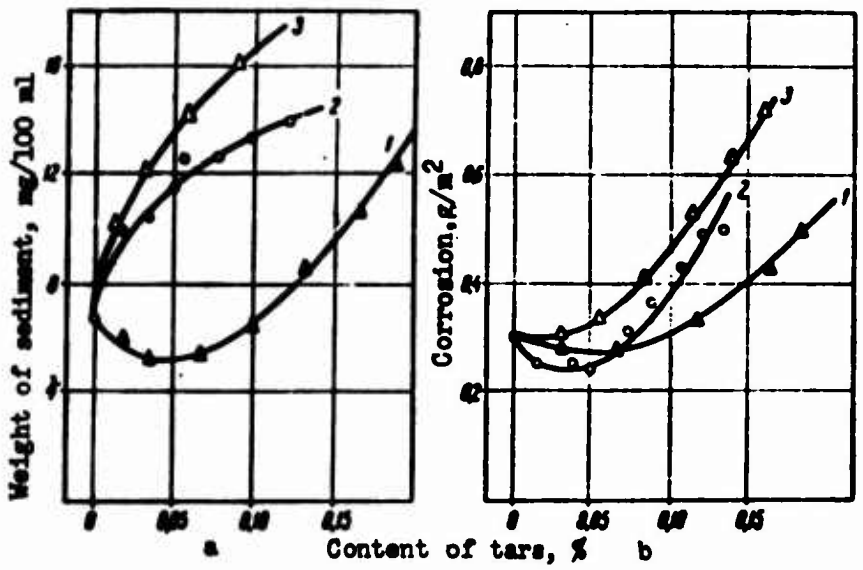

Fig. 67. Influence of tarry substances on stability (a) and corrosivity (b) of fuel TS-1. 1 – tars isolated from fresh fuel TS-1; 2 – tars separated from preliminarily detarred fuel after one year's storage; 3 – tars separated from twice-detarred fuel after a year's storage.

On the Mechanism of Formation and Enlargement of Particles of Sediment Insoluble in Fuel

The parent fuel, after separation of mechanical impurities, can be considered to be a true solution of heteroorganic compounds in hydrocarbons. Solid particles are lacking in such fuel. Solid particles (sediment) appear only after prolonged storage of fuels or with their heating in the fuel systems of aircraft. We will consider in greater detail the process of formation and enlargement of sediment insoluble in fuel.

The great inclination of sulfur-, oxygen-, and nitrogen-containing compounds to oxidation is well-known. Unsaturated hydrocarbons are also easily oxidized. These components are oxidized considerably more intensely than the basic hydrocarbon part of the fuel. Such oxidation occurs at the expense of oxygen of the air with which the fuel is in contact.

Initially there occurs an increase in the molecular weight of heteroorganic compounds, at the expense of oxygen, and subsequently there is condensation and polymerization of the products of oxidation of unstable impurities of the fuel. The homogeneous system which we had in the beginning is turned into a heterogeneous colloidal system. Such a colloidal system is characterized first by the presence of very small particles, with dimensions of 10 to 2000 A.

Depending upon the chemical nature of the heteroorganic compounds of the fuel, these particles can consist of various numbers of molecules. It is necessary to

note that molecules already subjected to the oxidizing attack of oxygen participate in such initial unification. The polarity and dipole moment of such oxidizing molecules are especially great. These small particles usually have a definite electrical charge.

The appearance of the electrical charge of the particles is explained as follows. With contact of two phases, on the boundary between them there usually appears an electrical potential, in connection with the formation of a double electrical layer. The cause of the appearance of the electrical potential consists in the fact that the surface molecules of a colloidal particle, dissociating, send into the solution ions of one sign while ions of the opposite sign remain on the surface of the particle.

Dissociations obviously are undergone first by molecules with ionic bonds (mercaptides, sulfide, metals, etc.).

After the formation of the initial particles of comparatively small dimensions (to 2000 A), there is observed their subsequent coagulation. Coagulation of small particles into bigger ones increases considerably during changes in temperature, concentration, etc.

The coagulation of particles is strongly affected by an external electrical field. In real fuel systems, especially at raised temperatures, there is frequently observed the appearance of different electrical fields. The so-called thermoelectric currents, which are caused by the heating of two contacting metals, appears especially frequently [41]. It is obvious that molecules having high polarity, great dipole moment, and an active functional group will promote the enlargement of the formed insoluble sediment. It is precisely this that explains the considerable enlargement of sediment in the presence of mercaptans. Mercaptans have the extremely active group —SH which, besides, causes high polarity of the molecule. Mercaptans actively interact with metals, especially with copper, with the formation of the corresponding mercaptides. Mercaptides subsequently can dissociate into ions, which is very important for the formation of a double electrical layer of colloidal particles.

In our experiments, after an hour's heating of hydrogenated fuel T-1 with addition of 0.01% secondary octylmercaptan small particles were formed (Fig. 68); the process of their coagulation could be observed in the microscope. Thus after 2-hr heating of the fuel we observed further consolidation and coagulation of small particles (Fig. 69). Final stage of the formation of insoluble sediment in the presence of secondary octylmercaptan is presented in Fig. 70. The large, dense particles were formed after approximately 3-4 hours of heating.

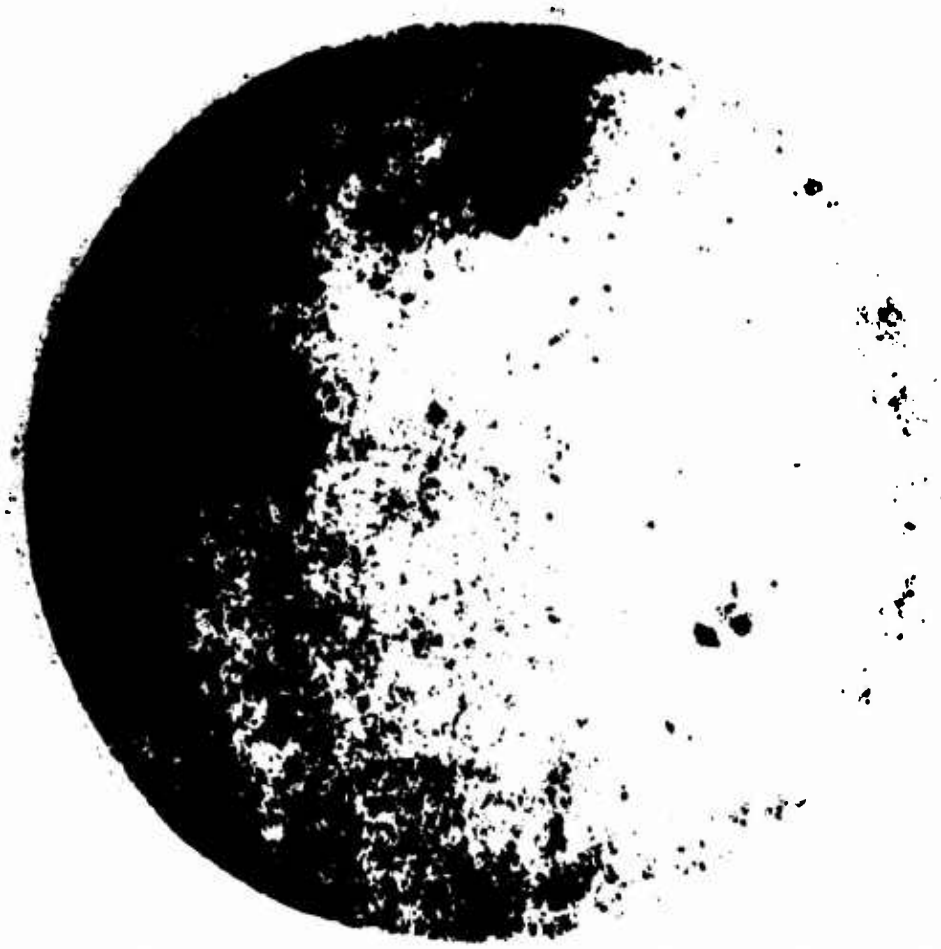

Fig. 68. Photomicrograph of coagulating particles of sediment formed after heating for one hour of fuel containing 0.01% secondary octylmercaptan.

Fig. 69. Photomicrograph of sediment formed after 2-hr heating of fuel JP-1 containing 0.01% secondary octylmercaptan.

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GRAPHIC NOT REPRODUCIBLE

Fig. 70. Photomicrograph of final stage of formation of sediment in the presence of 0.01% secondary octylmercaptan.

In sulfides the atom of sulfur is shielded by hydrocarbon radicals; therefore, in their presence coagulation of particles of insoluble sediment is observed in a smaller degree.

In disulfides the two atoms of sulfur are also shielded by hydrocarbon radicals, but the bonds between the atoms of sulfur are nondurable. At a temperature of 150°C and above the disulfides start to disintegrate, with formation of mercaptans and hydrogen sulfide [45], which causes intensive sedimentation.

Confirmation of the varied effect of sulfur compounds with different structures can be found in the results of a study of the elemental composition of sediment. When the fuel contains few sulfur compounds (Tables 58 and 59) the organic part of the sediment includes small quantities of sulfur and the total amount of sediment is insignificant, containing little ash. With the addition of sulfur compounds (primarily mercaptans) processes of sedimentation are sharply intensified and the content of ash and sulfur in the composition of the sediment is increased. The composition of the ash includes considerably increased amounts of copper, antimony, phosphorus, and other component parts of the metals which the fuel contacts in the

process of heating.

Table 58. Elemental Composition of Sediment Insoluble in Fuel, %

Elements	Fuels					
	Hydrogenated TS-1	Hydrogenated TS-1 + 0.01% secondary octyl-mercaptan	Hydrogenated TS-1 + 0.01% thiophenol	Hydrogenated TS-1 + 0.1% α-octyl-thiophene	Hydrogenated TS-1 + 0.1% α-octyl-thiophane	Hydrogenated TS-1 + 0.1% isohexyl-phenyl sulfide
Composition of organic part:						
Carbon	42.82	36.35	31.08	41.52	40.08	41.22
Hydrogen	4.38	3.72	4.29	4.11	4.38	4.49
Sulfur	0.25	6.71	8.43	2.17	3.18	4.42
Nitrogen	Traces	Traces	Traces	Traces	Traces	Traces
Oxygen	49.35	41.82	43.40	47.82	48.07	44.04
Ash	3.20	11.40	12.80	4.30	4.29	5.83
Composition of ash (in % on sediment):						
Aluminum	0.01-0.03	0.01-0.03	0.001-0.003	0.01-0.03	0.01-0.03	0.01-0.03
Magnesium	0.001-0.003	0.01-0.03	0.003-0.001	0.001-0.003	0.01-0.03	0.001-0.003
Calcium	0.01-0.03	0.01-0.03	0.1-0.3	0.01-0.03	0.001-0.003	0.001-0.003
Iron	0.01-0.03	0.01-0.03	1-2	0.01-0.03	0.01-0.03	0.01-0.03
Manganese	0.001-0.003	0.001-0.003	0.001-0.003	0.01-0.03	0.01-0.03	0.01-0.03
Nickel	0.001-0.003	0.003-0.01	0.03-0.1	0.001-0.003	0.001-0.003	0.01-0.03
Titanium	0.010-0.03	0.003-0.03	0.001-0.003	0.001-0.003	0.001-0.003	0.001-0.003
Chromium	Res.	0.3-1.0	0.3-1.0	0.1-0.3	0.1-0.3	0.1-0.3
Copper	1-2	3-10	3-10	1-3	1-3	1-3
Lead	0.01-0.03	0.001-0.003	0.01-0.03	0.001-0.003	0.001-0.003	0.003-0.01
Antimony	0.01-0.03	0.03-0.1	0.001-0.003	0.01-0.03	0.03-0.1	0.03-0.1
Zinc	0.3-1.0	3-5	3-10	0.3-1.0	1-3	0.3-1.0
Tin	0.01-0.03	0.03-0.1	0.001-0.003	0.01-0.03	0.01-0.03	0.003-0.001
Phosphorus	Res.	0.1-0.3	0.3	Res.	Res.	0.3

Table 59. Elemental Composition of Sediment Insoluble in Fuel, %

Elements	Fuels					
	Hydrogenated fuel TS-1 + 0.1% diiso-sec-heptyl sulfide	Hydrogenated fuel TS-1 + 0.1% diphenyl disulfide	Hydrogenated fuel TS-1 + 0.1% di-sec-octyl disulfide	TS-1	T-1	DA
Composition of organic part:						
Carbon	39.01	33.34	33.98	28.99	32.11	30.00
Hydrogen	4.09	3.83	4.58	5.00	5.96	5.83
Sulfur	6.00	7.29	7.83	8.91	6.01	6.83
Nitrogen	Traces	Traces	Traces	0.39	1.08	1.72
Oxygen	45.15	51.51	47.37	49.52	46.63	46.24
Ash	5.75	6.03	6.24	7.19	8.21	9.38
Composition of ash:						
Aluminum	0.01-0.03	0.01-0.03	0.01-0.03	0.01-0.03	0.01-0.03	0.003-0.01
Magnesium	0.003-0.001	0.03-0.01	0.003-0.01	0.03-0.1	0.03-0.01	0.03-0.1
Calcium	0.1-0.3	0.3-1.0	0.3-1.0	0.3-1.0	0.3-1.0	0.3-1.0
Iron	0.003-0.01	0.03-0.1	0.01-0.03	0.003-0.001	0.03-0.1	0.03-0.1
Manganese	0.003-0.01	0.003-0.01	0.03-0.1	0.001-0.003	0.01-0.03	0.01-0.03
Nickel	0.03-0.1	0.03-0.1	0.1-0.3	0.001-0.003	0.03-0.1	0.03-0.1
Titanium	0.01-0.03	0.001-0.003	0.01-0.03	0.001-0.003	0.001-0.003	0.003-0.03
Chromium	0.1-0.3	0.1-0.3	0.01-0.03	0.1-0.3	0.1-0.3	0.1-0.3
Copper	3	1.0-3.0	1-3.0	1.0-3.0	3-5	3-5
Lead	0.03-0.1	0.003-0.01	0.03-0.1	0.003-0.01	0.01-0.03	0.01-0.03
Antimony	0.1-0.3	0.03-0.1	0.1-0.3	0.03-0.1	0.1-0.3	0.1-
Zinc	0.1-0.3	0.3-1.0	0.1-0.3	0.3-1.0	0.3-1.0	0.3-
Tin	0.01-0.03	0.003-0.01	0.01-0.03	0.003-0.01	0.003-0.01	0.003-

The effect of sulfur compounds (other things being equal) is determined by their structure and concentration.

The content of oxygen in the composition of sediment is great – it attains 50%; therefore it is impossible to explain its presence only by the participation of the oxygen compounds of the fuel in the formation of sediment. Sediments are products of deep oxidizing transformations of unstable components of the fuel, especially sulfur compounds. Oxidation flows at the expense of atmospheric oxygen and is complicated by processes of consolidation of products up to gums and then to solid formations. These processes occur especially intensely in the presence of metals, which not only accelerate sedimentation catalytically but also participate actively in these processes (Table 60).

Table 60. Composition in wt. % of Insoluble Sediment Formed During Heating of Commercial Fuel TS-1 in Contact with Various Metals, wt. %

Designation of elements	Composition of insoluble sediment formed in the presence of		
	bronze VB-24	duralumin D1T	steel 12KhN3A
Carbon	28.99	27.09	26.96
Hydrogen	5.96	8.38	9.62
Sulfur	6.01	7.48	7.80
Nitrogen	1.08	0.39	0.73
Ash	8.21	4.35	4.81
Ash elements:			
Silicon	0.3-1.0	0.3-1.0	0.3-1.0
Aluminum	0.3-0.1	1-3.0	0.3-0.01
Magnesium	0.3-0.1	0.03-0.1	0.3-1.0
Calcium	0.3-1.0	0.3-0.1	0.03-0.1
Iron	0.003-0.01	0.3-1.0	1-3.0
Manganese	0.001-0.003	0.001-0.003	0.01-0.003
Titanium	0.001-0.003	0.1-0.3	0.01-0.03
Copper	3-10	0.01-0.03	0.001-0.003

The composition of sediment formed in fuels during their heating in contact with various metals includes many elements which are basic constituent components of the metallic alloys used. Thus, during heating of fuels in contact with bronze much copper is found in the ash; in contact with steel, considerable quantities of iron; and, finally, in contact with duralumin, large quantities of aluminum.

In formation of insoluble sediment in fuels, besides sulfur and other heteroorganic compounds, unsaturated hydrocarbons and ash elements existing in the fuel play a very active role. This is confirmed by the detection in the composition of the ash part of formed insoluble sediment of a large part of the ash elements of the parent fuels. Extremely small particles of the products of corrosion of metals and ambient dust penetrate into the fuels and, as it were, form centers around which

particles of high-molecular heteroorganic compounds aggregate. Removal of ash elements from the composition of fuels would lead to a considerable decrease in the processes of sedimentation.

Ways to Increase Thermooxidizing Stability of Jet Fuels

We can outline the following means of improving the thermooxidizing stability of jet fuels.

1. Technological purification of fuels of low-stability components (in the first place, unsaturated hydrocarbons and the majority of heteroorganic compounds).
2. Creation of fuels of special chemical composition.
3. Improvement of properties of fuels with the help of additives.
4. Preliminary fine filtration of fuels.

Sufficiently stable fuels can be obtained with the help of technological methods of purification. For instance, with help of hydropurification we obtain from sulfurous crudes the hydrogenated fuel TS-1, with a total sulfur content of 0.01% and practically no other heteroorganic compounds and unsaturated hydrocarbons. This fuel has high thermooxidizing stability (after 6 hour's heating at 150°C 0.3-0.6 mg/100 ml of sediment was formed). In the United States sufficiently stable fuels are obtained by means of hydrocracking [30, 31]. These methods of increasing thermooxidizing stability can find wide application.

The creation of fuels of definite chemical composition can also be used to solve, to a considerable degree, the problem of increasing of thermooxidizing stability of fuels (Chapter III).

Increasing the thermooxidizing stability of jet fuels with the help of additives is one effective way to improve their operational properties. At present intensive studies are being conducted on the synthesis of new additives, usable up to at least 200-250°C.

A large number of additives have been developed and are used to increase the stability of petroleum products in conditions of prolonged storage at moderate temperatures.

They are divided into the following large groups:

— aromatic amines,

— aminophenols,

— phenols.

However, all known additives of such structure have turned out to be poorly effective at temperatures higher than 100°C. The majority of these additives, upon

heating, are subject to thermooxidizing transformations and will form insoluble sediment and gums.

Thus, to increase thermooxidizing stability of jet fuels, it would be necessary to synthesize new substances.

It is obvious that these additives must be polyfunctional, i.e., antioxidant, dispersive, anticorrosive, and antiwear.

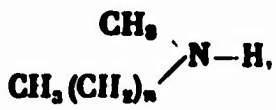
Reduction of the positive catalyzing effect of metals on the oxidation of fuels is attained by the formation of protective films by additives on metal surfaces. Such a function can be fulfilled by a substance having in its own composition polar groups (for instance $-SH$, $-OH$, $-NH$, $-NH_2$, and others). The part of the additive not consumed on the formation of protective films should, due to its specific structure, fulfill antioxidant functions.

If the anticorrosive and antioxidant properties are insufficient for effective prevention of sedimentation, the additive should still have dispersive properties.

The action of a dispersive additive can be explained by the formation around the first appearing, extremely fine sediment particles of shells of molecules of a surface-active additive, oriented with its polar group to the particle and the radical to the fuel. This shell will prevent further aggregation of fine particles into larger ones; the particle dimensions remain less than that of the filtering element mesh.

New additives should have high thermooxidizing stability and should dissolve well in fuel.

It has been established that aliphatic amines [15, 26, 32] essentially increase the thermooxidizing stability of fuels. The most effective are amines with the structure



where n = 12-15.

However, insoluble sediment and gums are formed during cooling of heated fuels with aliphatic additives [33].

F. N. Mazitova and Ya. M. Paushkin synthesized aminoalkyphenols [22] which decreased the formation of insoluble sediment in fuel T-1 by 2-3 times (Table 61).

As can be seen from the data, to recognize alkylphenols and aminoalkylphenols as sufficiently effective is impossible.

Table 61. Influence of Alkylphenols and Aminoalkylphenols on the Thermooxidizing Stability of Fuel T-1 at 150°C for 2 hr

Designation of additive	Concentration of additive, %	Sediment, mg/100 ml	Acidity, mg KOH/100 ml
Parent fuel.....	–	7.5	2.8
o-Amino-p-propylphenol ..	0.05	5.1	1.19
o-Amino-p-tert-butylphenol	0.012	3.9	1.43
o-Amino-p-tert-amylphenol	0.012	2.5	1.78
Dimethylphenol-m-amino-p-oxyphenylmethane	0.012	2.6	0.83
2.6-diamino-4-tert-butylphenol	0.05	2.0	0

Ashless additives of the type of polymers turned out to be good dispersive additives [27, 28, 34, 36].

Recent achievements in chemistry have allowed the obtaining of copolymers of assigned chemical composition. It is possible to introduce various groups with needed capabilities into the skeleton of the polymer. Such groups impart to the additive assigned properties: surface activity (hemosorption); lyophilic or lyophobic qualities; the ability to form protective films on metals, to render a dispersive action, to stabilize colloidal systems, to lower the freezing point, and so forth.

Copolymers are obtained as thermally stable and effective in a wide temperature range. If the composition of copolymers includes no metals or other inorganic elements, they are practically ash-free.

Several copolymer additives have been created. Copolymers of ethers of methacrylic acid have been obtained. Copolymerization of various methacrylic ethers, for instance primary aliphatic alcohols C_7-C_{15} and amino alcohols or methacrylic ethers of alcohols and 2-methyl-5-vinylpyridine styrene and other compounds which are inclined to polymerization, is carried out. At present a whole series of additives of the type of "acryloids" and "alkadines" is known. They are effective up to +200°C.

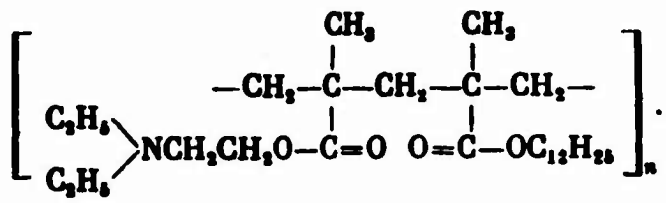
There are also known additives obtained on the basis of ethers [esters] of methacrylic acid and lauryl alcohol, octyl alcohol, diethylethanol amine, methacryl anilide, glycidil [?] methacrylate, 2-ethyl-hexyl methacrylate, N-(β-vinyloxyethyl formaldehyde), dodecyl styrole [37].

For instance, in the United States there is advertised the additive FOA-2 (Fuel Oil Additive) with the following properties:

Molecular weight	50,000
Density $\rho_4^{15.5}$	0.902
Flash point in an open crucible, °C	68
Viscosity, cs:	
at -17.8°C	6,000
at 0°C	1,800
at +25°C	540
at +37.8°C	329
at +98.9°C	65
Pour point, °C	-28.9

FOA-2 dissolves completely in hydrocarbons; it is insoluble in alcohol and acetone; less than 0.01% dissolves in water. The additive starts to decompose at 260°C and at 426°C is completely decomposed.

The schematic formula of additive FOA-2 can be expressed [39] as



Addition of 0.1-0.5% additive FOA-2 ensures thermooxidizing stability of jet fuels to a temperature of +204°C.

A deficiency of this addition is the fact that in its presence stable emulsions are formed between fuel and water.

Recently new additives have been synthesized which turned out to be very effective [19, 40, 44]. Data characterizing the action of the new additives are given in Table 62.

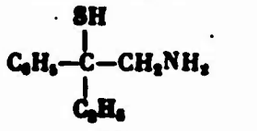
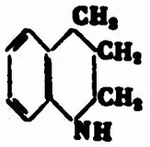
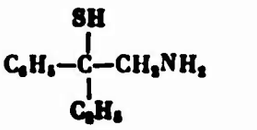
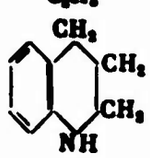
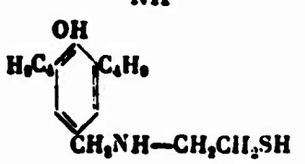
As can be seen from the data, the most effective compound turned out to be 2-phenyl-2-mercaptobutylamine. With a content of this additive of 0.05% the fuel after heating remains transparent and colorless and contains practically no insoluble sediment and gums.

It has been experimentally established that after preliminary filtration the stability of jet fuels is increased [46].

In Table 63 gives data characterizing the inclination to the formation of insoluble sediment of unfiltered and filtered fuels. Investigations were conducted on installations simulating real fuel systems of aircraft [47].

Unfiltered fuel is very inclined to form insoluble sediment, which clogs the filter in the first ten minutes of work.

Table 62. Influence of Certain Additives (0.05%) on the Thermooxidizing Stability of Jet Fuels at 150°C

Name of additive	Structural formula of additive	Sediment, mg/100 ml	Corrosion, g/m²	Deposits on bronze, g/m²	Optical density	Acidity, mg/100 ml
	Fuel TS-1					
—	Parent fuel	5.8	0.70	1.05	0.105	1.6
2-phenyl-2-mercaptobutylamine		0.3	0.1	0.1	0	0
1,2,3,4-tetrahydroxyniline [?]		0.8	0.4	0.2	0	0
3,5-ditertbutyl-4-oxybenzyl-2-mercaptoethylamine		0.7	0.3	0.2	0	0
Additive 63f	—	0.6	0.2	0.2	0	0
	Fuel TS-1 Parent fuel	7.2	1.1	1.3	0.83	2.8
2-phenyl-2-mercaptobutylamine		0.2	0.1	0.1	0	0
1,2,3,4-tetrahydroquinoline		0.9	0.3	0.6	0.020	0
3,5-tertbutyl-4-oxybenzyl-2-mercaptoethylamine's		1.6	0.6	0.3	0.025	0
Additive 63f	—	0.9	0.3	0.3	0.017	0

With an increase in the purity of the parent fuel the thermooxidizing stability increases. This confirms the earlier-stated position that during heating small particles existing in parent fuels promote the formation of insoluble sediment [5, 48].

Table 63. Influence of Preliminary Filtration on Formation of Insoluble Sediment Jet Fuels

Indices	Fuel with boiling range of 147-285°C			Fuel with boiling range of 200-341°C		
	Parent	Filtered through 30-40 μ mesh	Filtered through 8 μ mesh	Parent	Filtered through 30-40 μ mesh	Filtered through 8 μ mesh
	On the TST-1 installation at 150°C					
Test time, min	360	360	360	55	290	360
Pressure drop on filter, mm Hg	300	90	6	340	340	5
	On the TST-2 installation at 150°C					
Test time, min	90	165	190	30	45	45
Pressure drop on filter, mm Hg	340	340	340	340	340	340
	On the TST-1 installation at 200°C					
Test time, min	225	360	360	290	-	360
Pressure drop on filter, mm Hg	340	150	80	340	-	50
	On the TST-2 installation at 200°C					
Test time, min	-	170	240	65	140	360
Pressure drop on filter, mm Hg	-	340	340	340	340	120

Antiwear Properties of Jet Fuels

In units of friction and mated components of the fuel system of an air-breathing jet engine, the role of lubricant is executed by fuel transported from the tanks to the injectors of the combustion chamber. The lubricating properties of jet fuels are considerably poorer than those of specially prepared oils and lubricants. These properties for fuels deteriorate with lowering of their boiling point, lowering of molecular weight of the constituent hydrocarbons, and increase of vapor pressure. With an increase in the evaporation temperature the viscosity of fuels increases.

Lubricating properties drop during the transition from more to less high-boiling fuels. By this index commercial fuels can be arranged in the following order: T-5, T-1, TS-1, T-2. Fuel T-2 (wide fractional composition) has the poorest lubricating properties.

The service life of mechanisms depends on the wear of their rubbing parts.

Wear can develop because of intensive abrasion of metallic surfaces. At high temperatures and loads galling or seizing of precision friction pairs separated by minute gaps is possible. Sometimes crumbling or pitting in a thin surface layer of metal under action of repeated high loads is observed.

On the whole, wear of components of mechanisms can occur according to the following causes: mechanical abrasion, corrosion damage to the surface, and

penetration of microparticles, playing the role of abrasive, between friction surfaces [49].

The danger of mechanical wear is reduced to a minimum by high precision and thoroughness of treatment of mated surfaces of metal and also by their appropriate selection in terms of friction qualities.

Corrosion wear can be reduced to a minimum through the use of special steels and alloys of nonferrous metals, corrosion-resistant in a medium of fuels. The quality of fuels is controlled for corrosivity. The content of aggressive compounds in their composition is limited. Fuels are nonelectrolytes; consequently, in the absence of water corrosion of metals of an electrochemical character is also insignificant. Especially passive to corrosion is deep-cleaned fuel, free from unstable hydrocarbons and impurities of sulfur, oxygen, and nitrogen compounds. As was already indicated, the oxidation of these heteroorganic compounds, especially at raised temperatures and under the influence of copper and its alloys, leads to the formation of "acid" products, easily entering into chemical interaction with metals (mainly with nonferrous metals containing copper).

Abrasive wear for mated metallic surfaces working in the low-viscosity medium of fuels obviously presents one of the most serious dangers, inasmuch as it appears on ground of formation in fuel of a finely-dispersed solid phase.

In conditions of raised temperatures, aeration during shifting of fuel and contact with catalytically active metals accelerate the processes of oxidation of unstable compounds of fuels and the formation of a finely-dispersed solid phase, owing to tarry substances, moisture, and mineral microimpurities with "ash" elements. Starting from particles with dimensions characteristic for colloidal systems (less one micron), under the influence of physical factors there occurs their enlargement. In one milliliter of fuel one can usually count hundreds of particles with dimensions of less than five microns which, besides being material for subsequent coagulation, play the role of abrasives, promoting wear of metallic friction surfaces. The danger in this phenomenon increases because along with sharp intensification of processes of formation of a solid finely-dispersed phase, with an increase of temperature viscosity and, together with it, the lubricating ability of fuels decrease.

With heating of the system a metallic friction surface in fuel has less and less protection. It is "bared" to intensive corrosion processes. As a result there is observed formation of deposits, representing a more or less durable film

on the surface of the metal, and consisting of tarry compounds and mineral components of the fuel and products of corrosion and wear of metals. Naturally such deposits strongly worsen friction conditions, decrease gaps of precision pairs and at high temperatures can lead to the impermissible phenomena of galling and even wedging. On the other hand, a "bared" surface of a catalytically active metal (copper, brass, bronze) intensifies the process of oxidation of unstable compounds of fuels and the formation of the solid phase.

Thus processes of wear of metals and impairment of thermal stability of fuels are interconnected. This is confirmed by the fact that almost all antioxidant additives and, all the more so, additives improving the thermal stability of fuels are simultaneously antiwear additives. The quality of additives is distinguished only on the basis of the temperature range of their effectiveness. Their role consists in protection of the metal through adsorption or chemosorption on its surface. This limits the destruction of the metal by corrosion processes and its catalytic effect on processes of oxidation in the fuel. On the whole the action of additives limits the formation in fuel of the solid finely-dispersed phase and the subsequent enlargement of its particles, and consequently lowers the danger of negative influence of the solid phase on abrasive wear of metals.

It is absolutely clear that if one were to prevent, by the introduction of an additive, the formation of sediment in fuel during heating, then simultaneously the antiwear properties of the fuel will be improved, corrosion processes (usually much intensified with temperature) will be limited, accumulation of gummy deposits adhering to metallic surfaces of mechanisms will be prevented.

Additives, as active substances, lower surface tension on the boundary fuel – metal. The majority of surface-active materials are characterized by a linear structure of molecules. Here one part of such linear molecules consists of groups related in their properties to molecules of fuel – in other words, of lyophilic groups; another part of the molecules consists of radicals which differ sharply in their properties from the hydrocarbons of fuel – lyophobic groups. These groups possess high polarity and sharply expressed valence forces [50]. The latter is a necessary condition for "covering" the surface of metal with a monomolecular layer of additive, with polar groups turned to it. As regards the lyophilic hydrocarbon radical, it ensures solubility of such additive in the fuel. Thus, an antiwear additive in fuel, being strongly adsorbed on rubbing metallic surfaces, as it were insulates the metal from the fuel, excluding or limiting their mutual disadvantageous

influence. The most effective antiwear additive will be one in whose presence in the fuel the wear of friction pairs at raised temperatures will differ as little as possible from wear in the same conditions but at ambient temperature. The permissible working range between temperatures will be the standard measure of the quality of an antiwear additive.

Naturally, antiwear additives must meet all requirements for fuel additives, namely:

— to dissolve well in fuel, giving a homogeneous mixture in a wide operating temperature range;

— to render no noticeable influence on the physicochemical characteristics of fuels;

— to be combined with additives for different purposes without a drop in effectiveness;

— to be introduced into fuels in minimum quantities;

— not to lower the burning properties of fuels;

— not to lose effectiveness in conditions of prolonged storage of fuels.

In the work of G. I. Kichkin, I. V. Rozhkov, et al. [51] it is shown, for instance, that an additive of the phenol type, FCh-16, playing the role of an antioxidant in fuels at comparatively low temperatures, is simultaneously an effective antiwear additive for fuel T-2 bringing its quality by this index close to that of fuel TS-1 without an additive [50]. In a certain temperature range the role of antiwear additive in fuel is fulfilled by: α-naphtol; N, N'-di-sec-butyl-p-phenylene diamine and 2.6-di-tert-butyl-cresol [51].

The appraisal of the wear of a mechanism is usually produced by the method of micrometric measurement of parts after operation in specially set conditions. This process requires thoroughness and is quite complicated. The selection by this method of effective additives and the appraisal of the antiwear properties of fuels are hampered. In this case help has arrived in the form of the laboratory stand KV-1, developed by K. I. Klimov and A. V. Vilenkin [52].

The stand KV-1 constitutes a friction machine with a friction pair, one of whose elements is a rotating spiral coil of wire fastened on the generator of a surface of a disk, and the second element is a motionless cylindrical roller. The friction pair is placed in a bath with a sample of the tested fuel (350 ml). Heating up to 150°C can be realized.

There is determined the magnitude of load P_k(kg) at which in test conditions (speed v, 0.7 m/sec; diameter of disk, 64 mm; pitch of turn of wire, 4 mm; diameter

of roller, 5 mm; diameter of wire, 2 mm; material, steel) there occurs destruction of the boundary layer and catastrophic wear of the friction pair begins.

On this stand at a temperature of 20°C the following limit values of P_k for fuels, in kg, have been obtained:

T-1.....25.3-30
TS-1..... 14-21
T-2.....10.8-15.9

It turned out that at a temperature of 135°C fuel TS-1 has poorer antiwear characteristics than fuel T-2 at 20°C, while fuel T-1 in the same conditions is close to T-2 [52].

From the presented material, it follows that antiwear properties of fuels depend on:

– temperature conditions of operation of the system friction pair – fuel;

– viscosity and limits of distillation of fuels;

– content in fuels of unstable hydrocarbons and nonhydrocarbon impurities, and also their inclination to oxidizing-consolidating transformations;

– the content in fuel of microcontaminations, including compounds with "ash" elements (soil dust, products of wear and corrosion of metal);

– the composition the metals and alloys from which the friction pair is made;

– thoroughness of treatment of surfaces and gaps;

– magnitude and character of loads (constant, variable) and operational conditions of work of mechanisms.

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CHAPTER VII

EVAPORATION AND COMBUSTION OF JET FUELS

General Characteristic of the Working Process of Jet Engines

The work of air-breathing jet engines is based on the formation of a gas-air flow. The energy of this flow is used to create jet thrust and, in compressor engines, and for the operation of the gas turbine of a compressor. The gas-air flow in air-breathing jet engines is formed in combustion chambers, where fuel is burned in a flow of air.

In compressorless engines the air is fed into the combustion chambers by means of impact pressure and in compressor engines, by a powerful air compressor. For rated engine operating conditions the air pressure at the inlet to the combustion chamber is 5-10 kg/cm^2.

The injection of fuel is carried out most frequently by swirlers. The cone of the jet of atomized fuel for various engines oscillates in quite wide limits, from 40 to 80°, and is selected in accordance with the type, form, and dimensions of the combustion chamber. Pressure of injection of fuel is varied, depending upon the operating conditions of the engine and attaining 40-60 kg/cm^2 and above on rated conditions at ground level.

The great surplus of air in turbojet engines is conditioned by the need to limit the temperature of the gas proceeding into the turbine, in order to ensure its reliable operation. The maximum permissible temperature of gases ahead of the turbine in contemporary engines is 880-930°C. Here the total coefficient of surplus of air is 3.8-4.5. At small loads and in conditions of high-altitude flight the coefficient of surplus of air is increased to 6-8 and more.

Before it enters the combustion chamber the air flow is braked to a speed not exceeding 40-60 m/sec and is divided into two parts. The smaller part proceeds directly into the zone of burning and ensures combustion of the basic mass of fuel with a coefficient of surplus of air close to 0.9-1.1. With this the temperature in the burning zone attains 1800-2000°C, which ensures stable burning. The larger part of the air flows around the front part of the fire tubes and, basically, on passing the burning zone is admixed gradually with the products of combustion. In the mixing zone, along with lowering and balancing of the temperature of the gas, there occurs also burning of products of incomplete oxidation and particles of unburned fuel, which may be carried partially out of the basic burning zone.

To increase stability of burning of the fuel, regions with return vortex flows of hot gas and air are created in combustion chambers. The average forward velocity of the gas-air flow in such regions does not exceed 15-25 m/sec.

An important feature of the working process of air-breathing jet engines is the simultaneous intense flow of process of carburetion, ignition, and combustion in conditions of a moving gas flow.

The thermal intensity [heat release rate] of combustion chambers of contemporary engines attains $200 \cdot 10^6$ kcal/m^3·hr and more.

Lowering the temperature and especially the pressure of air entering engine combustion chambers worsens conditions of ignition and burning of fuel promotes unstable burning, and under certain conditions can lead to extinguishing of the flame. Especially unfavorable conditions for the working process are created at great heights, at lowered pressure and temperature on the inlet and with a decrease in turbine rpm. With ascent air density drops and the mass flow rate of air, other things being equal, decreases. Preservation of the necessary temperature of gases ahead of the turbine leads to a reduction in fuel flow rate, which involves a decrease in injection pressure and impairment of the quality of atomization.

All this disturbs stability and lowers the completeness of combustion of fuel at great heights.

Let us consider the influence of basic operational factors on the completeness and stability of combustion of fuel in air-breathing jet engines.

Influence of air pressure. To guarantee completeness of combustion of fuel it is necessary that air pressure on the inlet to the combustion chamber of motor be more than 1.5 kg/cm^2. When pressure drops below this value there is observed

considerable lowering of the completeness of combustion. This is explained by the fact that with a decrease of pressure the rate of the chemical reactions of oxidation is lowered and the turbulence of the flow decreases, which lowers the burning rate. Besides this, a decrease in air pressure impairs the quality of atomization and distribution of fuel in the combustion chamber. All this reduces the completeness of combustion of fuel.

As an example, Fig. 71 shows the dependence of completeness of combustion of fuel on air pressure at the inlet to the combustion chamber; burning occurred at a coefficient of surplus of air equal to 6.

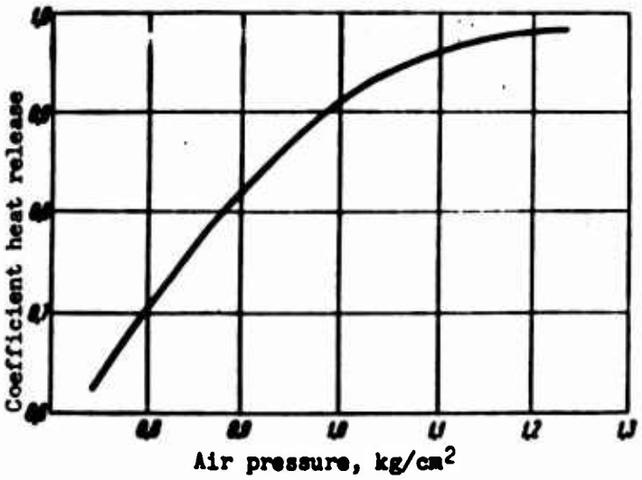

Fig. 71. Influence of air pressure on the inlet to the combustion chamber on completeness of combustion of fuel [28].

Due to the fact that with a decrease of air pressure on the inlet the conditions of carburetion and combustion are impaired, the region of stable burning is narrowed in conditions of a drop in pressure. This is especially strongly manifested in the region of lean mixtures.

Figure 72 gives dependences showing how the limits of stable burning of fuel vary with a change in aircraft altitude.

Influence of mixture ratio. For every combustion chamber there exists an optimum value of the coefficient of surplus of air at which the completeness of combustion of fuel is greatest. Deviation from this value in the direction of enrichment or leaning of the fuel-air mixture causes a decrease in the completeness of combustion. With an enrichened mixture burning occurs with a deficiency of oxygen and the conditions required for full carburetion, necessary for normal combustion, are not created. The cause of lowering of completeness of combustion with leaning of the mixture is a lowering of the burning rate. Part of the fuel-air mixture carried into the zone of mixing in practice does not burn, due to a lowering of the temperature because of cooling by the large quantity of air entering this zone for mixing and temperature balance. When there is a considerable deviation of the mixture ratio from the optimum value of the coefficient of air surplus in the direction of enrichment or leaning, the burning rate drops so much that flameout occurs.

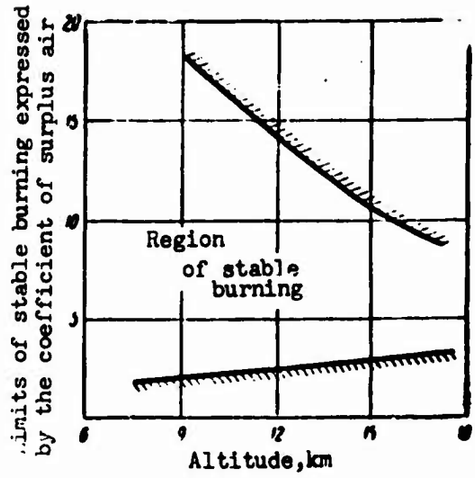

Fig. 72. Effect of altitude of aircraft on limits of stable burning of fuel in engine [28].

The effect of mixture ratio on completeness of combustion of fuels is shown in Fig. 73.

Effect of air temperature. With a decrease in air temperature the rate of evaporation of fuel and the rate of processes leading to ignition decrease. All this lowers the burning rate. The process of combustion cannot be completed in the burning zone and part of the unburned fuel passes into the mixing zone, where (as was shown above) conditions for realization of complete combustion do not exist.

Deceleration of carburetion and combustion with lowering of the air temperature also impairs the stability of combustion. A graph illustrating the effect of air temperature on completeness of burning is shown in Fig. 74. As can be seen from the graph, a sharp drop in completeness of combustion of fuel is observed at air temperatures lower than 80°C on the combustion chamber inlet.

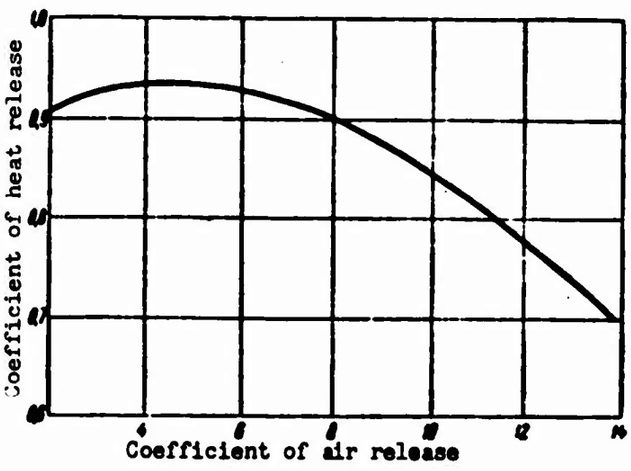

Fig. 73. Effect of mixture ratio on completeness of combustion of fuel [28].

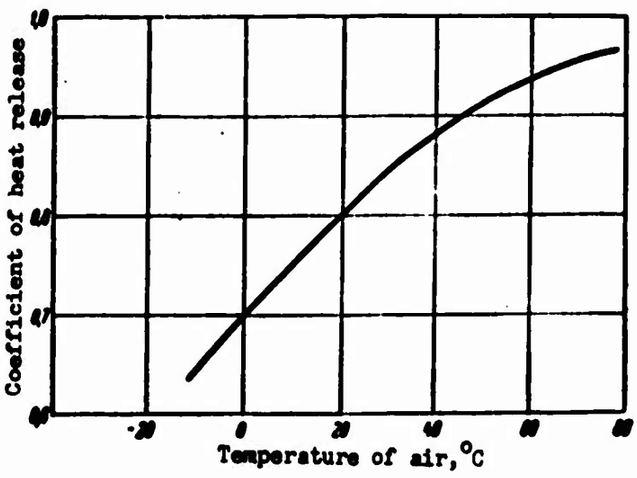

Fig. 74. Effect of the temperature of air at the combustion chamber inlet on completeness of combustion of fuel [28].

Effect of air speed. An increase in the air speed at the combustion chamber inlet increases the degree of turbulence and improves conditions of carburetion and combustion. However, at very great speeds of the gas flow in the combustion chamber, the time of stay of the fuel-air mixture in the burning zone can strongly decrease;

this will lead to a drop in completeness of burning. With a further increase in the flow rate, the transfer of heat and active reaction products from the burning zone into the fresh mixture will not correspond to processes of mixing and flameout will occur. With an increase in the speed of the air flow the region of stable burning is reduced.

Effect of quality of atomization. With a change in the operating conditions of the engine the pressure of injection of fuel and the pressure and speed of the gas flow in combustion chamber also change. This leads in turn to a change in the quality of atomization of fuel. With impairment of the quality of atomization and distribution of fuel in the combustion chamber the completeness of combustion is noticeably lowered.

Characteristics of the Processes of Evaporation, Ignition, and Combustion of Jet Fuels

Evaporation of Fuels

In the usual complicated complex of physicochemical transformations of fuel in air-breathing jet engines processes of evaporation occupy an important place. Along with atomization and the distribution of atomized fuel, the process of evaporation is one of the most important elementary processes of carburetion in engines. Ignition and combustion of fuels in air-breathing jet engines occurs in the vapor phase at a certain relationship between fuel and air, i.e., evaporation precedes ignition and combustion and to a considerable degree determines the character of these processes.

By its effect on the quality of carburetion, the process of evaporation indirectly affects the completeness and rate of burning of fuels in the engine.

Volatility is connected with the formation of vapor locks in fuel lines and the phenomenon of cavitation, affecting processes of supply to the engine and pumping of fuels (see Chapter V).

On the volatility of fuels depend losses during storage, pouring, filling, servicing, and other storage operations and also during application of fuel in a supply unit. Along with losses, impairment of the quality of fuel due to evaporation of its lightest components is possible. Volatility of fuels also affects the conditions at which the appearance of fire and explosions is possible.

Factors affecting rate of evaporation. The rate of evaporation ($dG/d\tau$) in the

general case is determined from the expression

$$\frac{dG}{d\tau} = \beta_p S (p_п - p_0) \text{ kg/sec},$$

[п = vap = vapor; 0 = en = environment]

where S is the surface of evaporation, m^2;

p_{vap}, p_{en} are the vapor pressure on the surface of evaporation and in the environment, respectively, kg/m^2;

β_p is the coefficient of evaporation, related to the difference of the partial vapor pressures on the surface of evaporation and in the environment, sec^{-1};

τ is the time of evaporation, sec.

The coefficient of evaporation β_p depends on the conditions of evaporation and the properties of the evaporated liquid. The coefficient of evaporation is usually determined by experimental data, on the basis of the theory of similitude.

During evaporation of fuel from a motionless surface in a medium of gas at rest the rate of evaporation is expressed by the amount of substance evaporated from a unit of surface in a unit of time:

$$q_{исп} = \beta_p (p_п - p_0) \text{ kg/m}^2 \cdot \text{sec}.$$

[исп = evaporated]

During static evaporation in conditions of free convection, taking into account the convection currents formed as a result of the distinction between the molecular weights of the evaporated substance and the medium, it is possible to take [4]

$$\beta_p = \frac{kD_p p_б M_п (Gr \cdot Pr)^{0.25}}{L(p_б - p_п)} \text{ sec}^{-1},$$

[б = b = barometric]

where k is an empirical coefficient;

D_p is the coefficient of diffusion, related to the gradient of partial pressures, m/sec;

p_b is the barometric pressure, kg/m^2;

Gr is the Grashof number;

Pr is the Prandtl number;

L is the length of the surface of evaporation of liquid, m;

M_{vap} is the molecular weight of the vapor.

During dynamic evaporation of fuels, especially in engine conditions, calculations of the rate of evaporation are very complicated. The rate of dynamic evaporation of atomized liquid fuels in the gas flow cannot be expressed by the quantity of substance evaporated in a unit of time from a unit of surface, inasmuch as the surface of evaporation is difficult to determine and changes strongly in the process of evaporation.

The rate of dynamic evaporation is estimated by the quantity of substance evaporated in a unit of time. In individual cases the rate of dynamic evaporation is expressed through the quantity of substance evaporated in a unit of time in a unit of volume of the space in which evaporation occurs.

The basic factors determining the rate of static evaporation are the properties of the evaporated fuel: pressure of saturated vapor, heat of evaporation, coefficient of diffusion, coefficient of thermal conductivity, heat capacity; and the conditions of evaporation: temperature of the fuel, pressure of the medium, and dimensions, form, and material of reservoir.

The literature contains no systematic theoretical study of the effect of these factors on the rate of static evaporation.

I. P. Budarov [5] introduces a number of particular dependences, allowing calculation of weight losses of various fuels for the most typical conditions of prolonged storage in surface, semiunderground, and underground reservoirs. At the basis of the calculations there is assumed an averaged temperature regime of the reservoirs, taken on the basis of experimental data.

During evaporation of atomized liquid fuels in a gas flow a great influence on the rate of dynamic evaporation is rendered by the quality of atomization, fuel speed, and the turbulence of the flow.

The effect of the quality of atomization on the rate of dynamic evaporation of fuels is manifested in several directions. First of all, depending upon the degree of atomization, the total surface of evaporation varies by tens and hundreds of times. The increase in the rate of evaporation with an increase of fineness of atomization occurs because of the increase in the pressure of saturated vapor with the increase in the curvature of drop surface and the reduction in the time of heating of drops.

With an increase in the curvature of the surface of evaporation, the pressure

of saturated vapor of the fuel increases in accordance with the equation

$$p_к = p_s + \frac{2\rho_ж \sigma}{98{,}1\,\rho_{пж} r},$$

[ж = liq = liquid; к = k]

where p_k is the pressure of saturated vapor above a convex surface of fuel, kg/m^2;

p_S is the pressure of saturated vapor at the same temperature above a flat surface of fuel, kg/m^2;

ρ_{vap}, ρ_{liq} are the densifies of the vapor and liquid, $kg \cdot sec^2/m^4$;

σ is the surface tension on the liquid – vapor boundary, kg/m;

r is the radius of curvature of the surface, m.

The quantity of liquid evaporated from the surface of a drop in a unit of time in an infinite volume of gas is

$$\frac{dG}{d\tau} = -4\pi r^2 \cdot D_c \frac{dc}{dr}.$$

Converting this equation, we obtain

$$q_{исп} = \frac{D_c C_s}{r} = \frac{D_p p_s}{r} \text{ kg/m}^2 \cdot \text{ sec},$$

where D_c, D_p are coefficients of diffusion related, respectively, to the gradient of concentrations and to partial pressures, m^2/sec and m/sec;

C_S, p_S are the concentration and pressure of saturated vapor at the surface of a drop, kg/m^3 and kg/m^2;

r is the radius of the drop, m.

The dynamic evaporation of atomized fuels is determined also by the homogeneity of atomization. With nonuniform atomization the rate of evaporation in the initial stage is considerably higher than that during uniform atomization; in subsequent stages the reverse is true. The time of full evaporation during nonuniform atomization is greater than that during uniform atomization.

The rate of dynamic evaporation, as was already indicated, is greatly influenced by the speed of the gas flow and its turbulence.

The aerodynamic action of the gas flow on the stream of atomized fuel leads to splitting of drops into smaller ones, thanks to which the surface of evaporation is increased. The breakaway of the vapor envelope from the surface of evaporating drops and mixing accelerate the processes of diffusion and, thereby the rate of evaporation.

In turbulent flow the transfer of substance is determined not by molecular diffusion, but by such characteristics of the flow as pulsational speed and the scale of turbulence, with an increase of which the rate of evaporation increases.

During evaporation of atomized fuels the pressure and temperature of the medium affect not only the change in the physical properties of the fuel but also the characteristics of the turbulent flow. With an increase in pressure and a decrease in temperature the pulsational flow rate is increased.

Besides these factors, during dynamic evaporation of fuels the rate of evaporation is affected also by such properties of the fuel as viscosity, surface tension, thermal conductivity, and heat capacity. Viscosity and surface tension of fuels affect the quality of their atomization, while thermal conductivity and heat capacity determine the time of heating of drops of fuel.

Methods of direct calculation of evaporation of drops of fuel moving in a flow of air are complicated, since it is necessary to consider the influence of very many factors [8, 10-12].

During evaporation of atomized fuel processes of heat and mass transfer flow simultaneously. An attempt at the theoretical calculation of the mutual influence of the processes heat and mass transfer at large differences of temperatures and partial pressures was made by Akkerman [14]. He showed that the coefficient of evaporation β_p' during joint flow of the processes of heat and mass transfer and large differences of partial pressures is connected with the coefficient β_p during separate process and with small differences of partial pressures by the relationship $\beta_p' = k_\beta \beta_p$.

According to D. N. Vyrubov, with temperatures of the ambient air of up to 200°C the value of the correction factor k_β differs little from unity. At a temperature of 700°C it is 0.93 at atmospheric pressure and 0.97 at a pressure of 4 atm (abs).

Therefore, for calculation of evaporation in conditions of simultaneous flow of processes of heat and mass transfer it is possible to use experimental data obtained at small differences of partial pressures and the separate process [8, 12, 13].

The results of such investigations are usually given in the form of criterial dependences:

for heat exchange

$$Nu = \frac{\alpha x}{\lambda} = f(Re; Pr)$$

and for mass transfer

$$Nu = \frac{\beta_p x}{D_p} = f(Re; Pr).$$

where α is the heat-transfer coefficient, kcal/m^2·hr·deg;

β_p is the coefficient of evaporation, related to the difference of partial pressures, sec^{-1};

λ is the coefficient of thermal conductivity, kcal/m·hr·deg;

x is the characteristic dimension (diameter of drop), m;

Nu is the Nusselt number.

During calculation of evaporation of individual drops of fuel, the magnitude of the coefficient of evaporation is determined as

$$\beta_p = \frac{D_p}{x} Nu,$$

and the rate of evaporation as

$$\frac{dG}{d\tau} = \frac{D_p}{x} Nu\, S(p_n - p_0) \text{ kg/sec.}$$

Integration of this equation gives the dependence of the change of dimensions of a drop in time

$$x_\tau^2 = x_0^2 - k\tau,$$

where x_0 is the diameter of the drop at the initial moment, m;

x_τ is the diameter of the drop after the interval of time τ, m;

k is a proportionality factor, m^2/sec.

As an example, Fig. 75 shows the results of calculation of evaporation of drops of kerosene with various initial diameters (x_0 microns). Evaporation was conducted at an air temperature of 200°C, a pressure of 1 kg/cm^2, and a speed of air flow of 22 m/sec with the initial relative speed of drops in the air flow being 66 m/sec.

For calculation of the evaporation of a jet of atomized fuel one should know the total distribution curve of drops by dimensions. Such a curve can be given graphically or in the form of an approximate equation.

For simplification of calculation, the totality of the drops is divided into separate narrow groups, for which a common average diameter can be taken. This average diameter is used to calculate the degree of evaporation of the given group of drops.

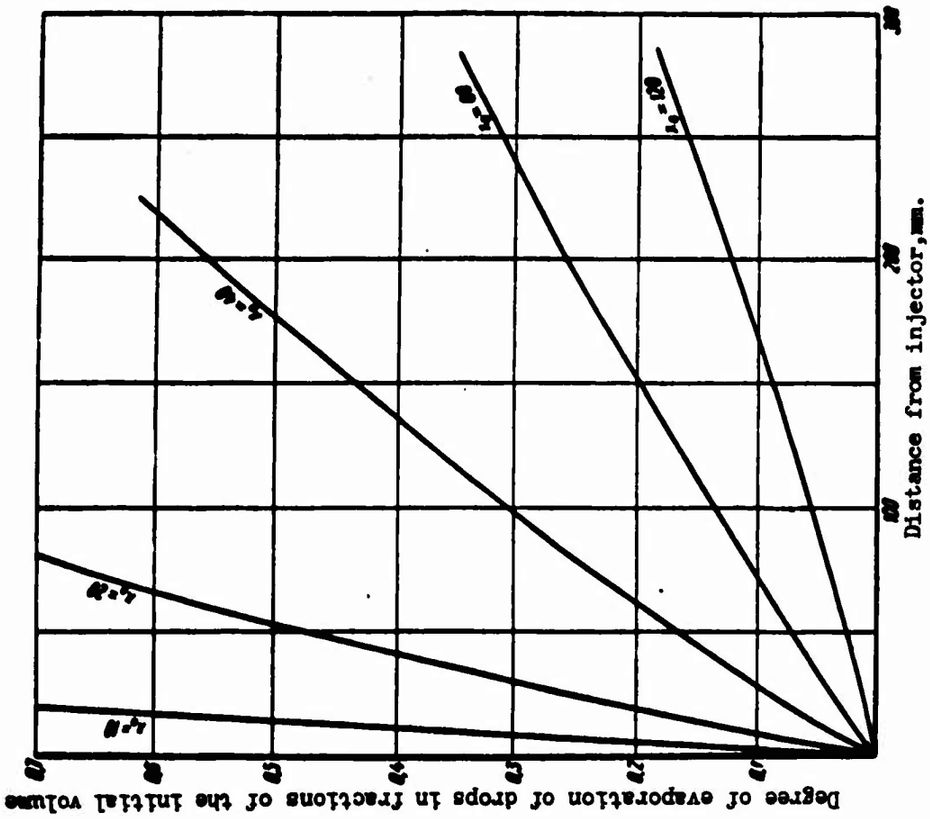

Fig. 76. Change in the degree of evaporation of drops of kerosene, depending on the distance from the injector (according to D. N. Vyrubov).

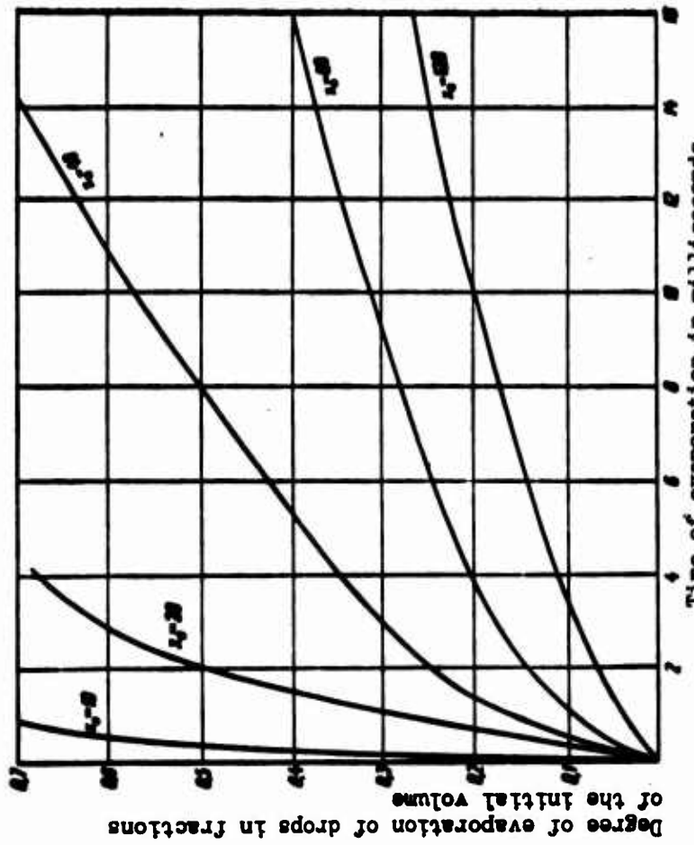

Fig. 75. Change in the degree of evaporation of separate drops of kerosene with time (according to D. N. Vyrubov).

The degree of evaporation of the entire jet is determined from the expression

$$\Omega_{\text{исп}}^{\Phi} = \sum \Omega_i V_i,$$

[Ф = j = jet]

where Ω_i, V_i are the degree of evaporation and the volume shares of individual groups of drops.

As an example, Fig. 76 shows the change in the degree of evaporation of separate groups of drops of identical diameter, depending on the distance from the injector. The conditions of evaporation are the same as in the experiments of Fig. 75. Knowing the volume share of separate groups of drops in the whole jet, we determine the degree of evaporation in the jet of atomized fuel with the help of similar graphs.

Ignition and Combustion of Fuels

Among the complicated physicochemical processes proceeding in the combustion chambers of air-breathing jet engines, the process of burning plays a determining role. The rate and completeness of the burning of fuel determine the stability and reliability of engine operation and also engine thrust and economy. The study of the basic regularities of the development of processes of ignition and combustion of jet fuels is of value not only for improvement of the working process of engines but also for the organization of their storage and transportation. Knowledge of the fire and explosive characteristics of jet fuels permits eliminating the possibility of fires and explosions during their treatment.

The process of burning is always carried out in the flame front, representing a zone of definite thickness in which the transformation of the chemical energy of the fuel into thermal energy occurs. The flame front separates the region of still nonreacting initial mixture from the region of products of combustion.

An important combustion characteristic is the speed of propagation of the flame along the fuel mixture.

In a laminar flow there will be formed a smooth and clear flame front, the speed of whose shift in the direction perpendicular to its surface is called the normal or fundamental speed.

In conditions of turbulent mixing of the fuel mixture, the flame front is distorted, its surface is increased, and under certain conditions it is disrupted;

then the observed flame consists of many foci. The shift of the flame front during turbulent burning in the direction perpendicular to its surface is called the turbulent speed of flame propagation.

Numerous experimental investigations have established that the speed of propagation of a turbulent flame (w_t) increases with an increase in the normal speed of flame propagation w_0 and the pulsational speed of gas flow w'. In the general form this dependence has the form

$$w_т = (w_0)^m (w')^n.$$

[т = t = turbulent]

The value of the exponents m and n depends on the conditions of burning and primarily on the character and intensity of turbulence.

For the case when $(w'/w_0) > 1$, the value of n is of the order of 0.6-0.8 and that of m, 0.2-0.4 (by experimental data).

The burning rate q_{burn} can be expressed as the quantity of fuel mixture burning in a unit of time from a unit of surface of the flame front. In this case it is determined by the formula

$$q_{гор} = w_т \gamma_{см} \text{ kg/m}^2 \cdot \text{sec},$$

[гор = burn = burning; см = mix = mixture]

where w_t is turbulent speed of flame propagation, m/sec;

γ_{mix} is the specific gravity of the fuel mixture, kg/m^3.

The burning rate can be estimated also by the quantity of fuel mixture burning in a unit of time in a unit of volume:

$$q_{гор} = \frac{w_т \gamma_{см} S}{V} \text{ kg/m}^3 \cdot \text{sec},$$

where S is the total surface of the flame front, m^2;

V is the volume of the combustion chamber, m^3.

Despite the fact that the process of burning is a chemical one, its rate is determined to a considerable degree by the physical processes of evaporation, mixing, and transmission of heat.

At present the theory of burning considers simple, particular forms of burning.

For instance D. A. Frank-Kamenetskiy [18, 19] developed the theory of microdiffusional burning in a turbulent flow. In microdiffusional burning, liquid fuel

in the vapor phase is broken into separate small volumes distributed in the flow of air. For such a form of burning the rate of the process is determined by the speed of mixing of the separate small volumes of evaporated fuel with the ambient air. Here the speed of propagation of the flame is directly proportional to the pulsational flow rate and, consequently, with constant intensity of turbulence, to the flow rate.

The assumption that during microdiffusional burning the burnup time is determined by the process of mixing and is absolutely independent of the kinetics of the chemical reactions in the flame front is justified so long as the time of the flow of the chemical reactions is considerably less than the time of mixing. With a decrease in the speed of reactions and in the time of mixing, the burning rate will be determined not by the time of mixing, but by the time of the chemical reactions, and will not increase with an increase in flow rate.

With the injection of liquid fuel into a turbulent flow of air there will be formed a two-phase fuel-air mixture in which, along with evaporated fuel, there exist drops of liquid fuel.

For characteristics of such a mixture it is necessary to have data on the dimension of drops of fuel in the mixture and also on the distribution of drops and evaporated fuel in the combustion space.

Works on the burning of two-phase mixtures are few at present and no definitive theory of this form of burning has been developed. Up to now the most detailed studies have been made of the question of the speed of burning out of individual drops with a purely conductive-diffusion mechanism of heat and mass transfer and at established temperature of the drop. In this case, around the drop there is established a spherical symmetric zone of burning, to which full vapors diffuse from the drop and oxygen from the surrounding space. The diffusion theory of burning of drops in these conditions was developed by G. A. Varshavskiy. The theory permits calculating the burning rate and burnup time of a drop, the dimension of the burning zone, and also the field of temperatures and partial pressures around the drop.

A number of works on the study of burning of two-phase fuel-air mixtures have shown that at a relatively low temperature of the fuel mixture and a small content in it of evaporated fuel, there is no continuous flame front and burning of separate drops of fuel and their totalities is observed. At high mixture temperatures there is observed a solid flame front and also foci of burning of separate drops of fuel

behind this front [20].

During burning of atomized fuel ignition of drops occurs due to propagation of heat from burning drops to unignited neighboring drops.

Calculations of the distribution of temperatures around separate drops of kerosene in motionless air performed on the basis of the diffusion theory of burning of drops without taking into account the dissociation of products of combustion show that at a distance of 30 drop diameters from its surface the temperature of the medium is equal to approximately 2200°C. Such a temperature reliably ensures ignition of the fuel-air mixture around neighboring drops.

Let us consider the effect on the burning rate of atomized fuels in a turbulent flow of such factors as the chemical composition of the fuel, the temperature, pressure, and turbulence of the gas flow, the quality of atomization of fuel, and the air-fuel ratio.

The properties of the fuel affect first of all the normal speed of flame propagation. In terms of normal speed of flame propagation hydrocarbons are arranged in the following order: alkanes < alkenes < alkadienes < alkynes [23, 24].

Cyclane and aromatic hydrocarbons have almost the same burning rate as alkanes, with the exception of benzene, whose burning rate is somewhat higher [1].

The effect of the structure and molecular weight of hydrocarbons on normal speed of flame propagation in mixtures of their vapors with air is shown in Fig. 77 [1].

Under ordinary conditions the maximum value of the normal speed of flame propagation for kerosene in mixture with air is approximately equal to 0.4 m/sec. A greater normal speed of flame propagation is observed for a mixture of hydrogen with air, where it attains 12 m/sec [1].

In fuel-oxygen mixtures the burning rate is considerably higher than that in fuel-air mixtures.

An increase in the temperature of the initial fuel mixture or of medium into which fuel is injected increases the burning rate.

With an increase in temperature the physicochemical processes of the formation of the fuel mixture and its preparation for ignition are accelerated. The normal speed of flame propagation is essentially increased (Fig. 78), although the pulsational speed of the gas flow is lowered. The dependence of the turbulent speed of flame propagation on temperature is expressed more sharply in a two-phase mixture

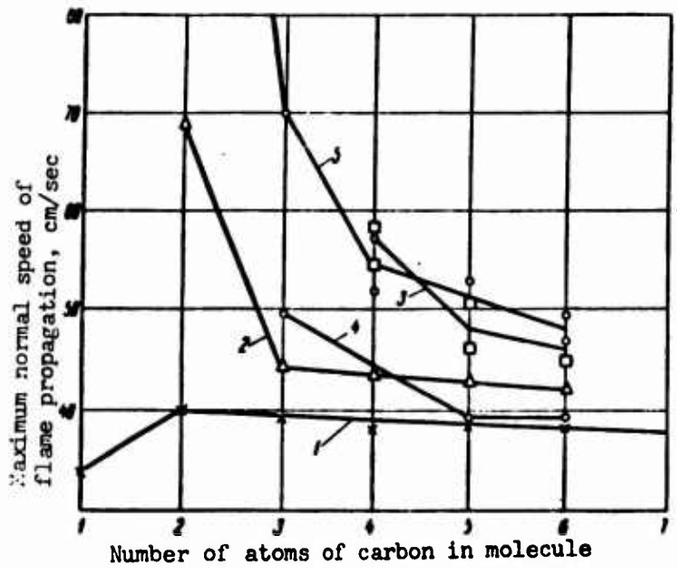

Fig. 77. Effect of structure and molecular weight of hydrocarbons on normal speed of flame propagation [1]. 1 — alkanes; 2 — alkenes; 3 — alkadienes; 4 — cycloalkanes; 5 — alkynes.

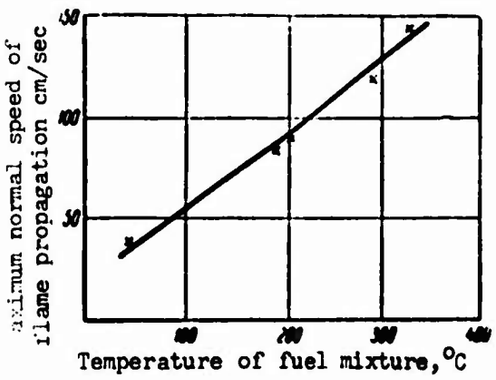

Fig. 78. Effect of temperature on normal speed of flame propagation of fuel T-1 mixed with air at a pressure of 400 mm Hg (after the Institute of Petrochemical Synthesis of the Academy of Sciences of the USSR).

than in uniform mixtures. Increase in the temperature of a two-phase mixture not only increases the rate of chemical reactions, but improves conditions for transmission of heat and substance and also increases the degree of evaporation of the fuel. The effect of mixture temperature on the burning rate of atomized fuels is shown in Fig. 79; the experiments were conducted with a flow rate of 20 m/sec and total coefficient of air surplus of 1.1.

Data available in the literature about the effect of pressure on burning rate are contradictory. It is known that with an increase in pressure (p) the normal speed of flame propagation (w_0) decreases. According to literature data, in hydrocarbon-air mixtures $w_0 \sim p^{-n}$, where n equals 0.23-0.35. At the same time the increase in the concentration of reactants and the closer contact between molecules of fuel and atmospheric oxygen caused by an increase in pressure accelerate the processes of oxidation and transmission of heat. With an increase in pressure the pulsational flow rate increases. As a result the turbulent burning rate (w_t) grows with an increase in pressure in the functional relationship $w_t \sim p^k$, in which the value of the exponent k is of the order of 0.25.

The turbulence of the medium has a very great effect on the burning rate. First of all, turbulence of flow determines the quality of the process of carburetion. With an increase in the intensity of turbulence of the flow the quality of mixing of fuel vapor with air is improved. Above it was indicated that in the case of diffusion burning, the speed of all process is determined mainly by the speed of mixing of fuel vapor and air.

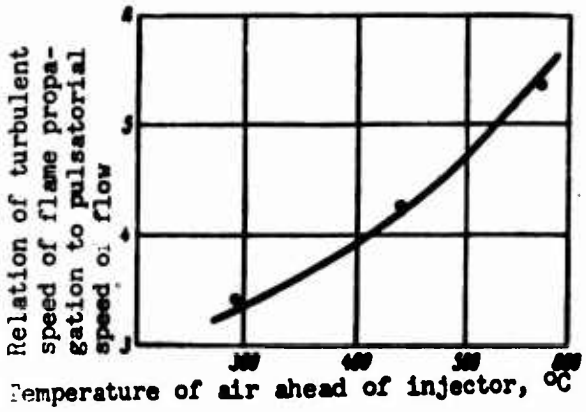

Fig. 79. Effect of mixture temperature on turbulent speed of flame propagation in two-phase mixtures (after B. P. Lebedev and V. G. Tikhomirov).

Turbulence affects the speed of flame propagation. Here it is necessary to distinguish two characteristic cases.

The first is the scale of turbulence, determined by the distance at which the displaced molar volume of fuel vapor, being mixed with the environment, is small as compared to the width of the burning zone. In this case the increase in the speed of flame propagation occurs because of intensification of processes of transfer of heat and matter by means of microturbulent pulsations in the burning zone itself.

The second case is that when the scale of turbulence is great in comparison with the width of the burning zone. Here there occurs an increase of the surface of the flame front and, consequently, in the burning rate.

The dependence of the turbulent speed of flame propagation on the pulsational flow rate (w') is shown on p.178 .

For instance, for a two-phase kerosene-air mixture with initial intensity of turbulence of about 3.5%, temperature of mixture of 310°C and variation of the flow rate in a range from 20 to 85 m/sec there is obtained the empirical expression (according to B. P. Lebedev and V. G. Tikhomirov):

$$w_т \approx 3{,}3\, w'.$$

Improvement of the quality of atomization increases the burning rate, owing to the increase in the speed of mixing, which is due mainly to the decrease of drops dimensions and the increase of evaporation and burning surface, as well as the additional turbulization of the flow during injection.

The effect of the air-fuel ratio on the speed of flame propagation can be seen in Fig. 80.

The maximum speed of flame propagation lies in region of enriched mixtures; for hydrocarbon fuels the maximum corresponds to a coefficient of air surplus of 0.8-0.9.

During burning of atomized liquid fuels it is necessary to distinguish the mixture ratio in the vapor phase directly ahead of the zone of burning and the mixture ratio which is estimated by the total coefficient of air surplus.

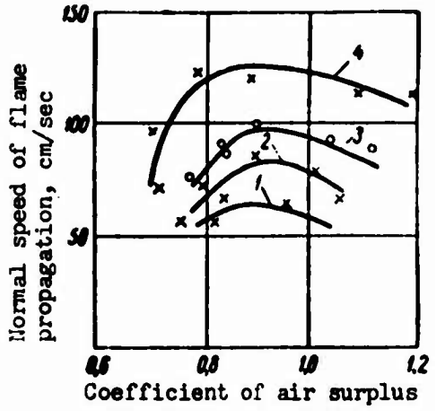

Fig. 80. Effect of mixture ratio on normal speed of flame propagation of fuel T-1 at a pressure of the fuel-air mixture of 500 mm Hg and various values of temperature (according to Institute of Petrochemical Synthesis of the Academy of Sciences of the USSR).

In two-phase mixtures the burning rate depends but little on the total coefficient of air surplus, since the magnitude of the latter affects the distance between drops and little changes the mixture ratio in the burning zone, where the process flows by a diffusion mechanism.

Figure 81 shows the effect of the total coefficient of air surplus on the speed of flame propagation in two-phase and single-phase fuel-air mixtures. On the graphs one can see that while for a single-phase mixture this dependence has a characteristic maximum of the speed of flame propagation with a coefficient of air surplus of 0.8, in the two-phase mixture the speed of flame propagation is reduced somewhat with an increase in the total coefficient of air surplus.

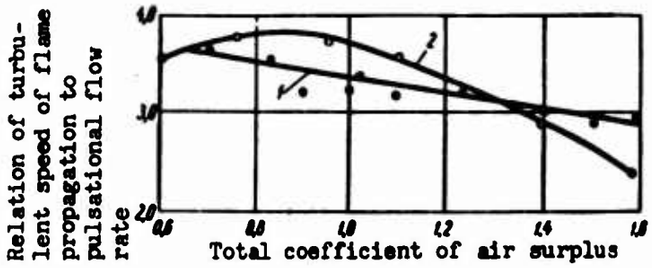

Fig. 81. Effect of mixture ratio on turbulent speed of flame propagation (after B. P. Lebedev and V. G. Tikhomirov). 1 — two-phase mixture; 2 — single-phase mixture.

Influence of Volatility of Fuels on Engine Operation

Insufficient volatility of fuels impairs combustion of the fuel-air mixture, increases scale formation, decreases engine thrust, and increases fuel consumption.

Good volatility of fuel is of especially great significance during starting of the engine and operation in low-temperature conditions. During starting of an engine in conditions of low temperatures of the external air the use of low-volatility fuel leads to difficulties caused by the impossibility of forming a fuel-air mixture lying within the limits of ignition.

Table 64 gives data characterizing the starting properties of a number of fuels,

Table 64. Starting Properties of Jet and Diesel Fuels

Fuels	Distillation limits, °C	Kinematic viscosity at 20°C cs	Pressure of saturated vapor at 38°C mm Hg	Optimum coefficient of surplus of air at which ignition occurs
T-2.....	78-237	1.09	100	5.8
TS-1	140-232	1.25	50	4.7
T-1	148-278	1.84	32	4.0
Diesel	185-355	4.47	-	2.8

obtained during tests on small-size engines. The appraisal of the starting properties of fuels was produced with a flow of air through the chamber of 0.1 kg/sec and air temperature at the chamber inlet of 60°C. As a parameter characterizing the starting properties we took the optimum composition of fuel-air mixture at which its ignition in combustion chamber occurs [9].

The lighter the fractional composition, the higher the pressure of saturated vapor, and the less the viscosity of fuel, the leaner the mixture at which ignition of fuel-air mixture in combustion chamber occurs and, consequently, the better its starting qualities.

Starting properties of jet fuels can be characterized by the temperature of distillation of 10% fuel. The lower the temperature at which 10% of the fuel is distilled, the easier it is to start engines and the lower is the feed pressure necessary to guarantee a quality of fuel atomization at which its sufficient evaporation and ignition occur.

Figure 82 shows the results of tests conducted on a small-size engine at an air temperature of 30°C and mass flow rate of air of 0.227 kg/sec.

In work [15] the following data are given: aviation gasoline, with a temperature of distillation of 10% of the fuel up to 71°C, ensures easy starting of engine at temperatures of the ambient air down to minus 55-60°C; during the use of a fuel with a temperature of 10% distillation up to 190°C, starting of the engine is hampered at an air temperature of minus 40°C. On a fuel with distillation limits of 240-365°C it was impossible to start the engine, although it worked on this fuel after being preliminarily started on kerosene. On heavier fuel, distilling within the limits 256-396°C, the engine did not work in these conditions.

To ease starting of engines of certain types, start fuels are used – unethylated

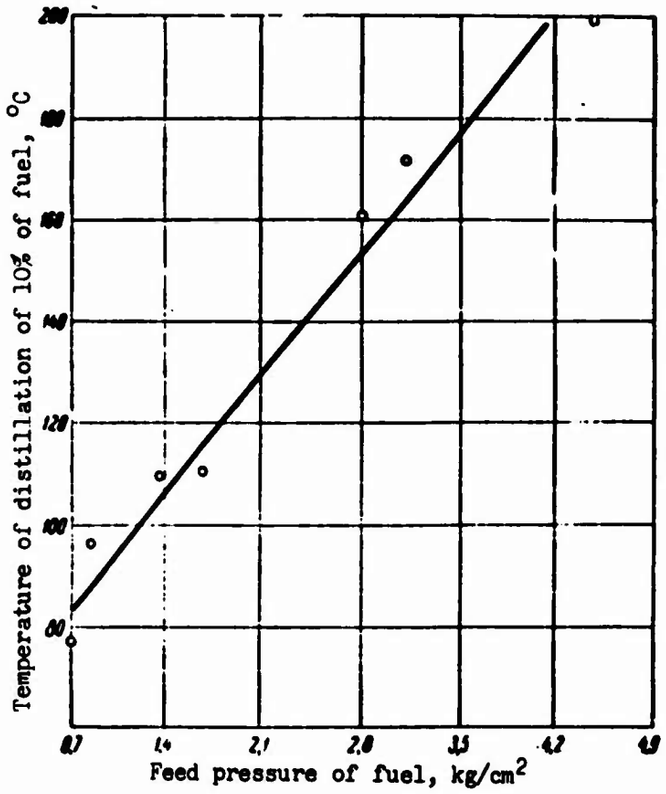

Fig. 82. Relationship between temperature of 10% distillation and the minimum feed pressure of fuel at which starting is possible.

gasolines in pure form or mixed with basic jet fuel or oil. For instance, for the engines of the TU-104 aircraft gasoline B-70 with addition of 1% MK-8 or transformer oil is used as a priming fuel.

Figure 83 gives starting characteristics of the fuels T-2 and T-1, taken on a full-scale combustion chamber at a temperature of the air on the combustion chamber inlet of minus 35°C [9]. As can be seen from the graphs, the starting properties of fuel T-2 are better than those of fuel T-1. Starting of an engine on fuel T-2 is possible at high speeds of air at the given height or at greater heights at a given air speed on the combustion chamber inlet.

Contemporary air-breathing jet engines at high flight speeds and during operation on rated conditions have high coefficients of heat release (0.95-0.98), but in unfavorable operating conditions the completeness of combustion can be noticeably lowered. The basic factors determining the completeness of combustion in a given engine design are the physicochemical properties of the fuel.

The lighter the fractional composition, the greater the pressure of saturated vapor and the lower the viscosity of the fuel, the higher will be the completeness of its combustion. With a change of ignition and burning conditions the influence of fuel properties is manifested unevenly. For instance, the heavier the fuel, the more strongly is the completeness of combustion reduced with impairment of the conditions of ignition and combustion, especially at great heights. Figures 84 and 85 show how completeness of burning of fuels of various fractional composition was changed with a change in the coefficient of air surplus and a change of air pressure on the combustion chamber inlet during tests on an installation with a small-size chamber.

Comparative characteristics of the completeness of combustion of jet fuel T-2

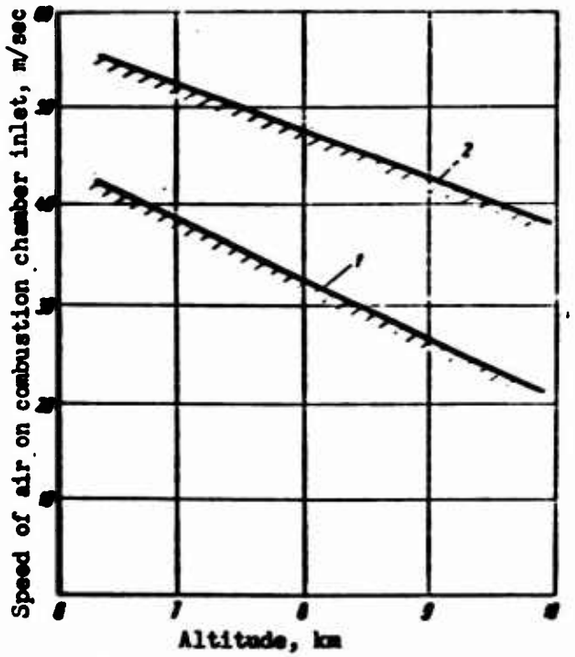

Fig. 83. Starting characteristics of fuels T-1 and T-2, taken on a full-scale combustion chamber [9]. 1 — fuel T-1; 2 — fuel T-2.

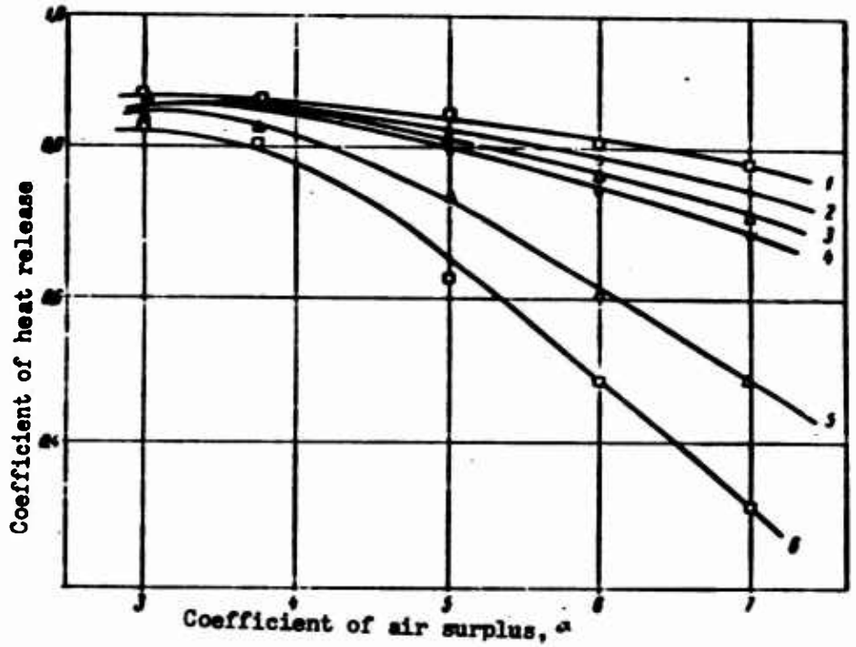

Fig. 84. Characteristics of completeness of combustion of various fuels [9]. 1 — gasoline B-70; 2 — fuel T-2; 3 — fuel TS-1; 4 — fuel T-1; 5 — heavy kerosene; 6 — diesel fuel.

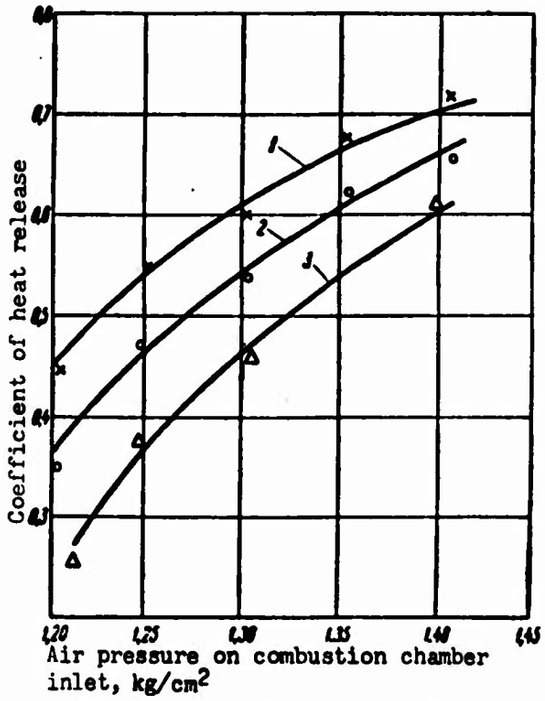

Fig. 85. Change in the coefficient of heat release, depending upon air pressure on the combustion chamber inlet (according to the author). 1 – gasoline B-70; 2 – fuel T-1; 3 – diesel fuel.

and gasoline B-70 in full-scale combustion chamber are presented in Fig. 86.

The characteristics of completeness of combustion of jet fuels T-1 (2) and T-2 (1), taken on the motor VK-1 in high-altitude conditions, are shown in Fig. 87.

The possibility of the formation of scale in the engine is intimately connected with the completeness of combustion of the fuel. The formation of scale on the walls of flame tubes of combustion chambers disturbs the aerodynamics of the flow, which impairs the quality of carburetion and the effectiveness of the use of fuel. Scale on the walls of flame tubes causes local overheating, which can lead to warping and cracking of the tubes. Particles of scale detached from the walls of the flame tubes transverse the gas flow and have a destructive action on turbine blades. Deposits of scale on the injectors impair the quality of atomization and consequently worsen the working process in the engine.

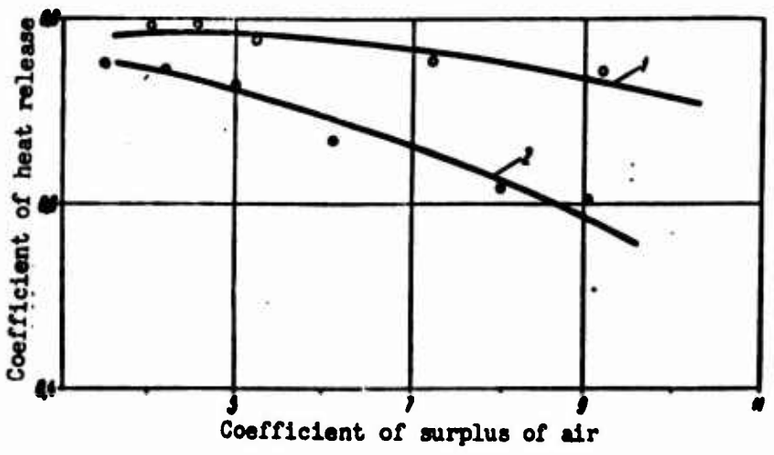

Fig. 86. Characteristics of completeness of combustion of aviation gasoline B-70 (1) and fuel T-2 (2) in high-altitude conditions [9].

The scale-forming ability of fuel depends on its volatility. Table 65 gives data on the scale-forming ability of a number of fuels. From the data in the table

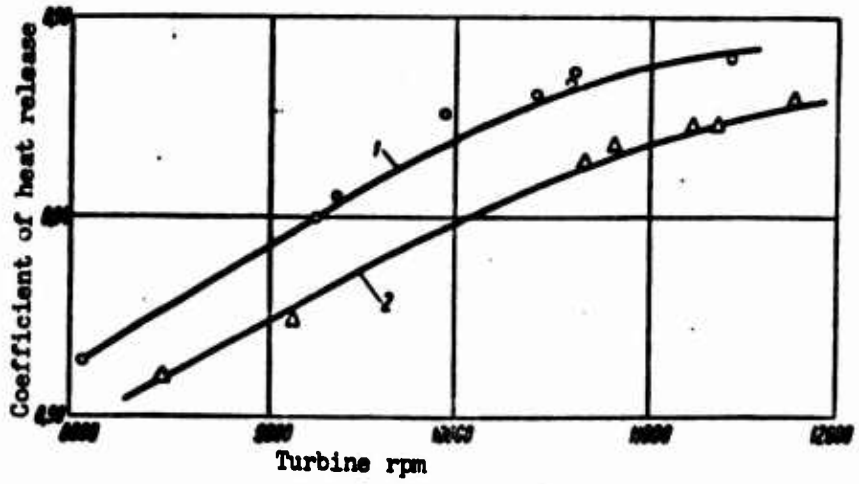

Fig. 87. Characteristics of completeness of combustion of fuels T-1 (2) and T-2 (1) [9].

Table 65. Scale-Forming Ability of Various Fuels During Tests on a Small-Size Engine [9]

Fuels	Quantity of scale in chamber	
	g	As % of scale formed during combustion of fuel T-1
Gasoline B-70	1.69	44
T-2	2.20	58
TS-1	2.90	76
T-1	3.80	100
Diesel	7.56	199

one can see that in terms of their inclination to scale formation, the various fuels are arranged in accordance with fractional composition; the lighter fuel, the fewer the deposits in the combustion chamber.

The inclination of jet fuels to scale formation during tests on full-scale VK-1 and RD engines is illustrated by the data in Table 66. The lighter of the fuels, T-2, gives less deposits of scale in the engi than fuel TS-1; during the burning of the latter, in turn, less scale will be formed than during the combustion of fuel T-1. In evaluating scale-forming ability, one should consider the group hydrocarbon composition of jet fuels, as it can exert a great measure of influence on this property.

Table 66. Scale-Forming Ability of Jet Fuels During Tests on Full-Scale Engines [9]

Fuels	Average weight of scale, g in one chamber after 100 hr of tests on engine	
	VK-1	RD
T-2	9.44	0.65
TS-1	14.44	1.33
T-1	-	2.06

From the table one can see that the quantity of scale formed is greatly affected by the design of the engine.

The volatility of jet fuels also affects the character of combustion in the engine. Normal combustion of fuel in air-breathing jet engines is characterized by a stable flame jet; burning occurs without pulsation, breakdowns, or extinguishing of the flame.

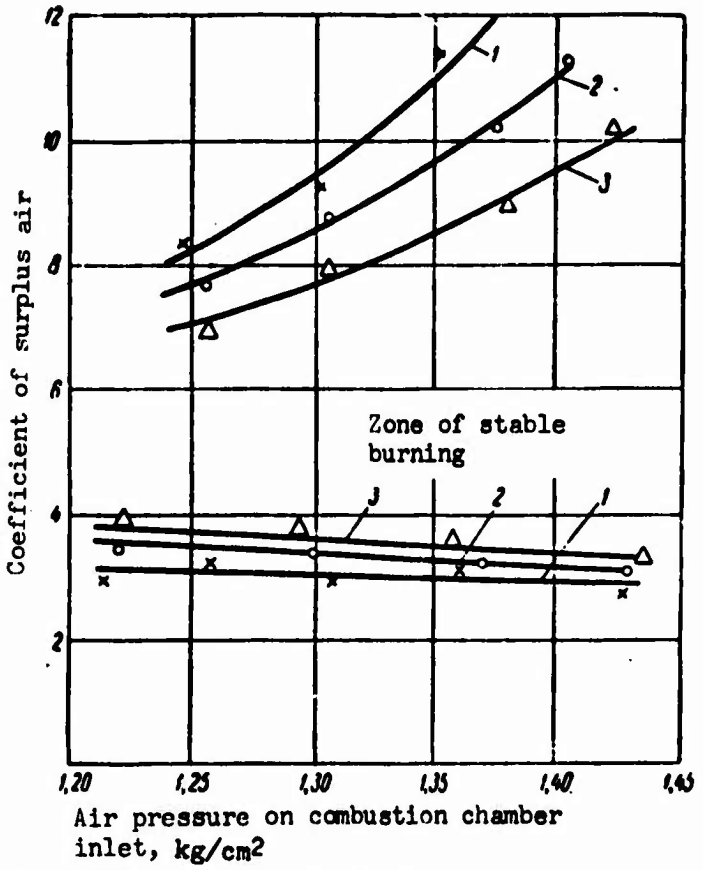

Fig. 88. Change in limits of stable burning of fuels, expressed by the limiting values of the coefficient of air surplus, depending upon air pressure on the combustion chamber inlet (author's data). 1 – gasoline B-70; 2 – fuel T-1; 3 – diesel fuel.

Flameout is the most dangerous disturbance of the normal process of combustion of fuel in the engine.

Flameout can occur with a very high speed of gas flow in the combustion chamber and also with a decrease of heat release in the burning zone. A decrease in heat release can be the result of lowering of temperature and pressure or of sharp leaning or enrichment of the fuel-air mixture entering the burning zone.

The volatility of the fuel affects the uniformity of the mixture ratio in the burning zone, and also the degree of leaning or enrichment of the fuel-air mixture with a sharp change in the engine regime.

With improvement of the volatility of jet fuels, the region of stable burning is expanded, mainly to the side of leaner mixtures. Besides volatility, the stability of burning depends on the quality of atomization and, consequently, on the viscosity and surface tension of the fuel.

The effect of the properties of fuel on the stability of burning during tests on an installation with a small-size combustion chamber is shown in Fig. 88.

Along with positive operational properties, fuels of lightened fractional composition have essential inherent deficiencies: a raised inclination to the formation of vapor locks, impairing the operation of fuel pumps; large losses by evaporation and lower volume heat of combustion, leading to a decrease in the range of operation of aircraft.

Losses of jet fuels during storage and transportation are comparatively small (Table 67).

The degree of influence of volatility on losses depends on the conditions of storage. For instance, the difference between losses of fuels of various volatility will be considerably larger in surface storage than in semiunderground and (all the more) underground storage. This difference in losses will be greater for small

Table 67. Loss of Fuel in 1 Month of Storage, in kg per 1 m^3 of Vapor Space, for Temperate Climatic Zone [5]

Conditions of storage	Fuels	
	T-1	Automobile gasoline A-66
Surface horizontal reservoirs:		
winter period	0.023	1.43
spring-autumn period	0.124	8.78
summer period	0.369	42.00
Surface vertical reservoirs:		
winter period	0.011	0.951
spring-autumn period	0.059	4.91
summer period	0.179	16.0
Semiunderground reservoirs:		
winter period	0.0067	0.614
spring-autumn period	0.023	2.16
summer period	0.055	5.42
Underground reservoirs:		
winter period	0.0034	0.192
spring-autumn period	0.0036	0.534

horizontal tanks than for vertical reservoirs of large capacity – and greater in southern zones than in the north.

According to I. P. Budarov [5], the average annual losses of fuel T-1 are 90 times less in vertical reservoirs and 100 times less in horizontal reservoirs than losses of automotive gasoline A-66.

Loss from evaporation in high-altitude conditions of fuels of the kerosene type, with distillation limits of 150-280°C, are insignificant up to heights of 18-20 km. With an increase in the pressure of saturated jet-fuel vapor losses from evaporation increase sharply (Table 68).

Table 68. Comparative Losses of Fuel at a Height of 18.3 km [1]

Fuels	Pressure of saturated vapor at 37.8°C kg/cm^2	Losses at initial temperature of fuel, wt.%	
		15.5°C	37.8°C
Kerosene	0.007	0.0	0.0
Fuel of wide fractional composition	0.136	0.0	1.0
The same	0.470	9.6	15.0

The loss of fuel in high-altitude conditions depends strongly on its initial temperature.

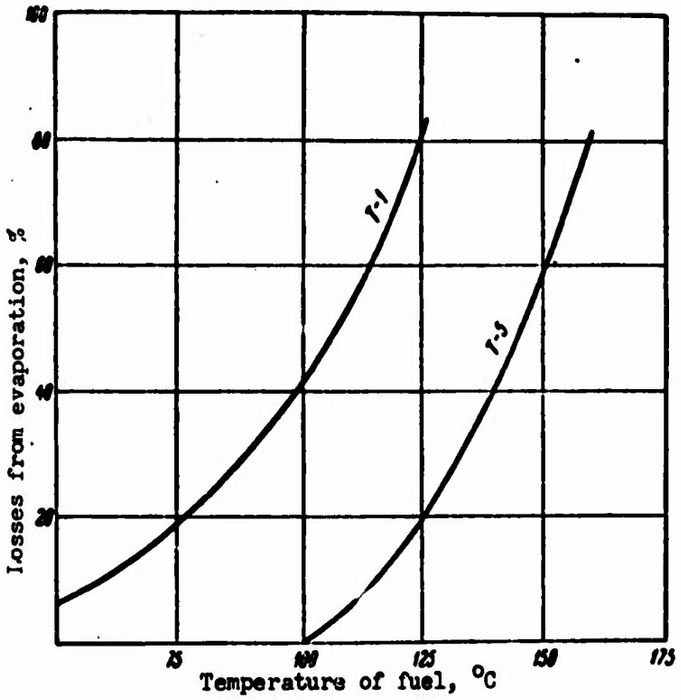

Fig. 89. Losses of jet fuels from evaporation, depending upon their temperature.

For aircraft with supersonic speed, in which the fuel can be heated to 100-150°C and move during flight, even fuels of the kerosene type will sustain quite considerable losses from evaporation and will form vapor locks unless pressure is created in fuel tanks.

For supersonic aircraft fuels are used which have higher initial distillation temperatures and smaller magnitudes of pressure of saturated vapor.

Figure 89 shows comparative characteristics of the fuels T-1 and T-5 in terms of their inclination to losses from evaporation at elevated temperatures. Use of fuel with high vapor pressure can be ensured if the fuel system will work under pressure and also with the installation of auxiliary pumps to preventing the formation of vapor locks in the fuel system of the aircraft. But the first measure increases the weight of the aircraft, on the average, by 40 g for every liter of fuel, and the second does not decrease losses of fuel from evaporation. Losses of fuel can be reduced by hermetic sealing of the tanks and cooling of the fuel on the ground. Hermetic sealing of fuel tanks increases the weight of the aircraft, and cooling of fuel on the ground requires additional equipment at airports.

The fractional composition of fuel is a factor in its heat of combustion. The range of operation of an aircraft depends on the reserve of fuel and thus, since the volume of the fuel tanks is limited, not only weight the heat of combustion per unit weight, but also that per unit volume of fuel is very important. With lightening of the fractional composition of hydrocarbon fuels and lowering of their density, the volume heat of combustion decreases noticeably. If the volume heat of combustion of gasoline is taken as 100%, the volume heat of combustion of kerosene-type fuel will be 110-115% and that of diesel fuel about 120%. It is necessary to note also that lightening of fuel improves its low-temperature properties.

Effect of Group Hydrocarbon Composition of Fuel on Engine Operation

The literature contains a limited amount of information about the effect of the group hydrocarbon composition of fuel on the work of air-breathing jet engines. This is explained by the fact that at present the practical possibilities of using fuels consisting chiefly of one hydrocarbon group (and all the more so of separate hydrocarbons) are limited.

With the usual forms of petroleum fuels the influence of their group hydrocarbon composition on the working process of air-breathing jet engines is manifested in smaller measure than the influence of volatility.

The starting properties of jet fuels are characterized by the limits of ignition by temperature and the period of delay of ignition. The best characteristics in this relation among the hydrocarbons are possessed by alkane hydrocarbons of normal structure with C_{10}-C_{16} carbon atoms in the molecule. Unsaturated hydrocarbons have wide limits of ignition.

However, alkane hydrocarbons of normal structure do not meet all requirements of pumpability, and unsaturated hydrocarbons fall short in stability; therefore they cannot serve as bases for the production of jet fuel.

Hydrocarbon fuels of the kerosene type and the wide gasoline-ligroin-kerosene fraction are close in terms of limits of stable burning in engines.

To expand the limits of ignition and increase the burning rate, the use of additives is proposed. For instance, to improve starting properties additives of the type of triethyl $Al(C_2H_5)_3$ and trimethy $Al(CH_3)_3$ aluminum [29] and diethyl ethers are recommended; to improve combustion, certain sulfur compounds: thiophene tar, tert-butylthrophene [31], and aluminum borohydride [32].

Investigations on a small-size motor, carried out in the Institute of Petrochemical Synthesis of the Academy of Sciences of the USSR under the leadership of F. A. Lavrov, have established certain dependences between group hydrocarbon composition of fuel and stability of combustion. On the installation with a small-size motor they tested fuels of the kerosene type with various group hydrocarbon compositions. The widest limits of stable burning are found in fuels of cyclane-alkane base with a small content of aromatic hydrocarbons. The narrowest region of stable burning in terms of mixture ratio is found in kerosene fraction of pyrolysis containing 79.6% aromatic hydrocarbons.

In our experiments on an installation with a small-size engine we obtained

analogous results. Tests were conducted on two fuels: T-1 and a 1:1 mixture of fuel T-1 and green oil (product of pyrolysis), having approximately the same fractional composition as fuel T-1 and containing 65% aromatic hydrocarbons.

On design and close to rated conditions of engine operation a change in the group hydrocarbon composition of the fuel has no large influence on completeness of burning. However, in less favorable conditions (for instance, with a decrease in pressure and temperature of air on the combustion chamber inlet and with a considerable increase in the coefficient of surplus of air) the effect of the chemical composition of the fuel is manifested quite strongly.

With large coefficients of surplus of air the temperature of the gases in the burning zone is lowered, which decreases completeness of combustion – especially with fuels with aromatic bases.

In conditions of low values of temperature and pressure and also with deceleration of motion of fuel and air, which takes place at great heights, the highest completeness of combustion is found in fuels with alkane and cyclane bases (characteristics of fuels are given in Table 69). This position is illustrated by the graph in Fig. 90, which shows the dependence of completeness of burning of fuels of identical volatility but different chemical composition on the altitude of the aircraft.

Table 69. Physicochemical Properties and Group Hydrocarbon Composition of the Fuels Whose Completeness of Combustion in High-Altitude Conditions Is Shown in Figs. 90 and 91

Fuels	Group hydrocarbon composition %			Distillation limits, °C	Kinematic viscosity at 37.8°C, cs	Density ρ_{15}^{15}
	Alkane	Cyclane	Aromatic			
Standard	41,4	39,2	19,4	155—271	1,54	0,791
Alkane base	92,2	5,2	2,6	150—265	1,30	0,748
Cyclane-alkane base	46,7	51,9	1,4	160—270	1,53	0,791
Aromatic base	13,4	11,4	75,2	166—253	1,16	0,865

The completeness of combustion of fuels of different group hydrocarbon compositions was compared with that of a standard fuel at a height of 6096 m [30].

Tests of the above-indicated fuels (Table 69) at various mixture ratios showed that fuels of alkane base ensure the best completeness of combustion at lower values

Fig. 90. Dependence of completeness of combustion of fuels of various group hydrocarbon compositions on altitude of aircraft [30]. 1 — standard; 2 — alkane; 3 — alkane-cyclane; 4 — aromatic.

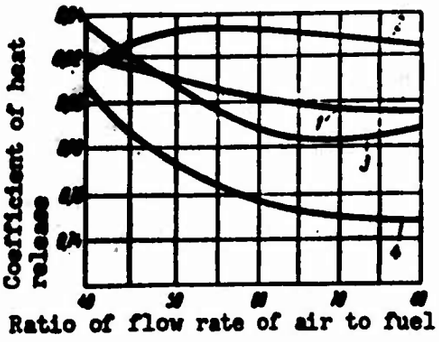

Fig. 91. Change of completeness of combustion of fuels of different group hydrocarbon compositions, depending upon mixture ratio [30]. 1 — standard; 2 — alkane; 3 — cyclane-alkane; 4 — aromatic.

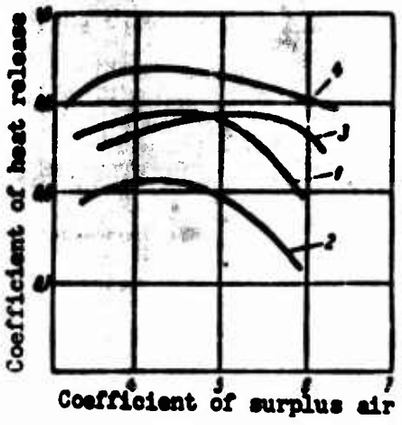

Fig. 92. Completeness of combustion of fuels. 1 — kerosene type, straight run distillation; 2 — kerosene type, thermal cracking; 3 — lightened, thermal cracking; 4 — lightened, catalytic cracking.

of the ratio of air and fuel than any others (Fig. 91).

Figure 92 presents the results of tests on full-scale engines of fuels obtained by straight-run distillation of crude and also by means of thermal and catalytic cracking (Table 70).

The kerosene fraction of thermal cracking, with a large content of aromatic hydrocarbons, had the least completeness of combustion. Lightened fuel from thermal cracking with a large content of unsaturated and aromatic hydrocarbons is inferior in completeness of combustion to kerosene-type fuel of straight run distillation on rich mixtures, but exceeds it on poor. The best characteristics in terms of completeness of combustion in all test conditions characterized fuel from catalytic cracking.

In analyzing the test results shown in Fig. 92, it is necessary to consider the influence of fractional composition. By comparing the characteristics of combustion of fuel samples 1 and 2, and then 3 and 4, it is possible to observe the influence of group hydrocarbon composition. During comparison of lightened fuels 3 and 4 with fuel of the kerosene type it is necessary to consider the different fractional compositions of the fuels.

The chemical composition of a fuel affects its heat of combustion. With an increase in the content of aromatic hydrocarbons in a fuel the volume heat of combustion grows, owing to the high density of aromatic hydrocarbons, although the heat of combustion per unit weight is lowered somewhat.

Table 70. Physicochemical Properties and Group Hydrocarbon Composition of the Fuels Whose Test Data (Full-Scale Engines) Are Shown in Fig. 92

Fuels	Group hydrocarbon composition, %			Distillation limits, °C	Density ρ_4^{20}
	Alkane and cyclane	Aromatic	Unsaturated		
Fuel of kerosene type	83.5	16.5	0	142-276	0.821
Fuel of kerosene type, thermal cracking ...	52	33	15	102-246	0.849
Lightened fuel, thermal cracking	45	25	30	60-240	0.780
Lightened fuel, catalytic cracking	68	25	7	46-241	0.780

Table 71. Scale-Forming Ability of Fuels of Different Group Hydrocarbon Compositions [30]

Fuels	Group hydrocarbon composition, %			Relative scale formation, %
	Aromatic	Cyclane	Alkane	
Standard	19.4	39.2	41.4	100
Cyclane-alkane base	1.4	51.9	46.7	70
Alkane base	2.6	5.2	92.2	10
Aromatic base	75.2	11.4	13.4	700

For instance, of the fuels shown in Table 69 at all test altitudes (Fig. 90), fuels on an aromatic base give the largest heat release per unit volume in spite of their lower completeness of combustion.

The literature contains a large quantity of data on the influence of the chemical nature of fuel on scale formation in engines [1, 2, 26, 27, 30].

In terms of scale formation, the various hydrocarbons are arranged in the following order: alkanes < cyclanes < monocyclic aromatics < bicyclic aromatics.

The effect of group hydrocarbon composition on deposit of scale in engines is clear from the data in Table 71.

The presence in fuel of sulfur compounds promotes scale formation; such scale possesses increased hardness and abrasive properties.

The content in fuel of existent gums in amounts of more than 20-30 mg/100 ml of fuel noticeably increases the formation of scale.

Investigations of influence of fractional and group hydrocarbon compositions

on the operation of air-breathing jet engines and experience in their operation have shown that the best (at present) are fuels with cyclane-alkane bases of the kerosene type, distilled at 150-300°C, with a content of aromatic hydrocarbons of less than 25%.

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