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By

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EFFECT OF SULFUROUS COMPOUNDS ON THERMAL STABILITY AND CORROSIVE PROPERTIES OF FUELS FOR TURBOCOMPRESSOR AIR-REACTIVE ENGINES

P. I. Davydov and G. F. Bol'shakov

In the fuel system of an engine the fuel may be subjected to changes, leading to deterioration of its exploitation properties.

One of the factors, deteriorating the exploitation qualities of a fuel in the fuel system of an engine, appears to be the rise in temperature.

In jet engines the fuel is heated in pumps to 20 - 30° and in fuel oil radiators - by 30 to 40° more. The fuel system as a rule, is mounted in the body of an air compressor, the temperature of which reaches in certain parts 200 - 250°. which causes additional hearing of the fuel.

Alreay in transport aircraft with turbojet engines of aircraft type TU-104, at cruising velocities of 800 - 1000 km/hr, there is observed a noticeable heating of the fuel.

Calculations show, that at a long last aircraft flight, at a speed of 1800 - 2000 km/hr, the temperature of the fuel will constitute 80° in the fuel tank, at the output from the oil radiator 130 - 150° and in the fuel pump 140 -160°.

In these conditions the fuel oxidizes intensively - tarry compounds and insoluble compounds are formed, plugging up the filters and depositing themselves in various parts of the fuel system. At higher temperatures the fuel being actively to corode the metals of the fuel system, especially copper alloys.

Formation of a residue accelerates at a temperature rise to 150 - 160°; and with further temperature rise - it decreases. Tar formation and corrosion action also have a maximum in the area of temperatures of the order of 170 - 180°.

An exclusive great value for corrosion processes of nonferrous metals of the fuel system and residue formation have sulfurous compounds. This is pointed out by the increase in sulfur content in the residue, comparative with its content in the fuel and the increase in the fractinn of the metal in residue, in proportion to the increase in content of sulfurous compounds in the fuel.

The investigations carried out by N. N. Torichnev have established, that alkane-cyclane fractions, separated from standard fuels TS-1, T-1 and T-5, do not contain sulfurous compounds and show no corrosive effect on bronze when heated to 150° for a period of 6 hours; in these fractions no residues form.

When adding to these fractions 0.08% (in conversion into sulfur) butyl-secondary octyl-sulfide in these conditions, 2.6 mg/100 ml of residue (sedimentation) is formed and corrosion of the bronze is observed (0.7 g/m^2). admixtures of diisoamylsulfide and dibutyldisulfide mixtures act somewhat more intensive.

Sulfurous fuel compounds are concentrated in its tarry and heavy aromatized part. Therefore, the detarring and dearomatization of fuels leads to a slowing down of corrosion processes and to a slowing down in residue formation during their heating. Together with our reports it has been revealed, that during the heating in the above mentioned conditions of aromatic fuel fractions, desorbed from silica gel with benzene and desulfurized, residue deformations are observed. Even a pure a-methylnaphthaline during heating for a period of six hours, separates a residue in the amount of 1-2 mg/100 ml.

These investigations have shown, that the basic corrosion and residue forming agents appear to be sulfurous compounds of fuels and, in a known measure, bicyclic aromatic hydrocarbons.

For a more detailed investigation of the effect of individual groups of sulfurous compounds on the corrosion of metals of the fuel system, the formation of residues in fuels during their thermal treatment, experiments were made with separation from fuels and with individually synthesized sulfurous compounds.

TC-1 fuel was taken for the investigation, obtained from petroleum from the Devonian horizon of the Mukhanovsk petroleum industry, subjected to hydro-purification at the installation of the Novo-Kuybyshev petroeum refining plant (experimental batch). The fuel contained 0.01% of general sulfur; mercaptanes were not discovered in the fuel. Individual sulfurous compounds and sulfurous fractions were added to this fuel, separated from TC-1 fuel and DA-Diesel fuel in an amount close to the content of sulfur in standard fuels.

Individual sulfurous compounds were presented to us by the Bashkir branch of the Academy of Sciences USSR. Sulfur and nitrogen containing individual compounds, were synthesized by F. Yu. Rachinskiy.

Separation of fractions of natural sulfurous compounds from the fuels was realized by the lab of Prof. R. D. Obolentsev by the absorption method, with subsequent extraction of acetic acid murcury through mercury complexes and by additional pruification with picric acid.

In the composition of natural sulfuric compounds, separated from TC-1 fuel, included are preferably alpphatic and aromatic sulfides, and also a certain amount of residual sulfur.

Sulfurous compounds, separated from Diesel fuel DA, contained 50% sulfides, 7 - 10% of disulfides and 40 - 43% of residual sulfur.

The basic physico-chemical properties of sulfurous compounds are listed in Table 1.

The investigation method was reduced to the following. The tested fuel in the amount of 150 ml was poured into the cylindrical vessel made from 12KHN3A steelwith a volume of 300 ml. Suspensions (g_1) were preliminarily placed in the fuel, a bronze plate from VB-24 with a total surface of 50 cm^2. After filling.the vessel was hermetiially covered and kept at 150° for a period fo six hours at continuous mechanical mixing (on account of oscillatory motion of the vessels).

After completion of the experiment, the fuel was cooled to room temperature and filtered through a glass filter No. 4. The residue was washed with petroleum ether and suspended. In the filtrate the acidity of the potentiometric method and the optical density were determined.

The bronze plate was washed with petroleum ether, dried in the air and suspended (G_2). The plate was then washed with an alcohol-benzene mixture (1 : 1), dried and again suspended (G_3).

The amount of depositions, insoluble in fuel, was calculated by the difference, G_2-G_3 in g/m². Corrosion of the bronze was determined as the difference G_1-G_3 in g/m².

Table 1.

Basic Physico-Chemical Properties of Sulfurous Compounds

Соединение 1)	Температура кипения (P, в мм рт. ст.) 2)	d_4^{20}	n_d^{20}	Молекулярный вес 3)	Содержание серы в вес. % 4)
Меркаптаны 5)					
Вторичный октилмеркаптан 6)	186/758	0,8440	1,4485	146	22,0
Меркаптотиозолин	—	—	—	—	—
2-фенил-2-меркаптобутиламин . . . . 7)	120/5	1,0567	1,5620	181	17,7
Сульфиды 8)					
Диизовторичный гептилсульфид . . . . . . 9)	263/760	0,8362	1,4538	230	14,0
Метилбензилсульфид . . 10)	212/760	1,0274	1,5630	139	23,0
Изогексилфенилсульфид . . 11)	249/760	0,9510	1,5245	194	16,5
Бутил вторичный октилсульфид . . . . 12)	254/760	0,8429	1,4580	202	15,9
Дивторичный октилсульфид 13)	315/760	0,8982	1,4818	290	22,0
Тиофаны 14)					
α-(2-метиламил) тиофан . 15)	234/757	0,9030	1,4798	172	18,6
α-(3-фенилпропил) тиофан 16)	209/760	1,0237	1,5518	206	15,5
α-гексилтиофан . . . . . 17)	219/748	0,9095	1,4826	172	18,6
α-октилтиофан . . . . 18)	245/751	0,8992	1,4793	200	16,0
α-(2-метилбутил) тиофан . 19)	212/757	0,9142	1,4820	158	20,3
Тиофены 20)					
α-октилтиофен . . . . 21)	261/748	0,9214	1,4919	196	16,3
Тиофен . . . . 22)	84/760	1,0614	1,5246	84	38,1
Сернистые соединения, выделенные из топлив 23)					
Сернистые соединения, выделенные из ТС-1 . 24)	205/240/760	—	1,4888	—	18,7
Сернистые соединения, выделенные из топлив ДА 25)	—	—	1,5200	—	11,5

(see page 5a for key to table)

Investigation results of the effect of sulfurous compounds on the corrosion properties and thermal stability of hydropurified TC-1 fuel are given in Table 2.

From the given data it is evident, that aliphatic mercaptanes in fuel at 150° cause sharp corrosion in bronze and intensify the condensation oxidizing reaction with the formation of soluble tars (increase in optical density), of tarry deposits on the metal and insoluble residue in the fuel.

Corrosion processes and oxidizing condensation processes become intensified with the increases in mercaptan content in the fuel. An increase in mercaptan content from 0.005*) to 0.01% intensifies corrosion by almost 9 times, residue formation - by 3 more times.

The forming insoluble residue contains sulfurous corrosion products of copper and of processes of deep oxidizing condensation of the fuel.

Bronze plates after being affected by fuel, containing mercaptanes, have a nonuniform, corroded surface (Figure 2). In Figure 1, for comparison, is shown a bronze plate after being affected by hydropurified fuel without mercaptanes.

The negative role of aliphatic mercaptanes appears also in the mixture with sulfurous compounds, separated from fuel. When 0.25% of these sulfurous compounts without mercaptanes are added to hydropurified fuel corrosion of bronze rose in double, residue formation - by 1.6 times, and when 0.24% of sulfurous compounds of 0.01% of secondary octylmercaptan was added to this fuel, corrosion rose by 7.5, and residue formation - by five times. Microphotography of the plate after being affected by hydropurified fuel with an addition of 0.24% of

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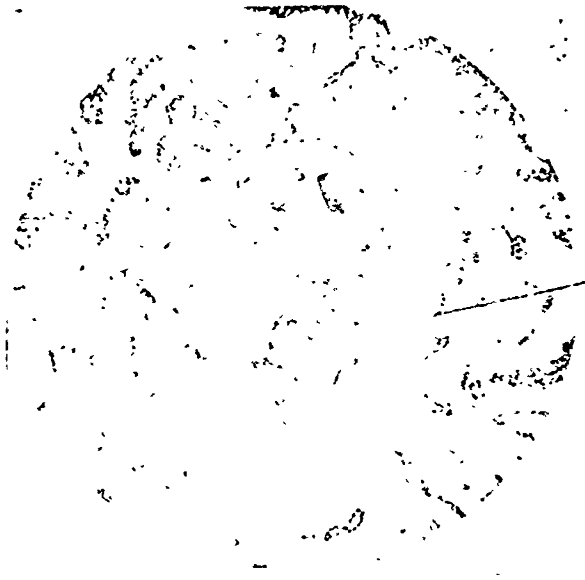
* In this case and in subsequent ones, the content of sulfurous compounds are expressed in weight % of sulfur in the fuel.

sulfurous compounds and 0.01% of octylmercaptan is shown in Figure 3.

Figure 1. Microphotography of a Bronze VB-24 Plate, Subjected to Heating in Hydropurified Fuel.

Figure 2. Microphotography of VB-24 Bronze Plates, Subjected to Hydropurified Fuel with an Addition of 0.01% of ptan.



GRAPHIC NOT REPRODUCIBLE

Figure 3. Microphotography of VB-24 Bronce Plate, Subjected to Heating in Hydropurified Fuel with an Addition of 0.24% of Natural Sulfurous Compounds and 0.01% of Secondary Octylmercaptan.

Table 2.

Effect of Sulfurous Compounds on Fuel Properties

Сернистые соединения 1)	Концентрация сернистых соединений, выраженная в содержании серы в топливе в вес. % 2)	Коррозия в г/м² 3)	Отложения на пластинке в г/м² 4)	Нерастворимые осадки в мг/100 мл 5)	Оптическая плотность после фильтрации 6)	Кислотность мг KOH/100 мл 7)
Исходное топливо 8)	—	2,0	2,5	2,2	0,020	1,83
Меркаптаны 9)						
Вторичный октилмеркаптан 10)	0,005	2,4	10,1	2,7	0,031	Отсут. absent
То же	0,010	20,4	21,3	8,5	0,102	»
» »	0,015	49,3	30,4	11,3	0,135	»
» »	0,020	60,9	33,5	12,2	0,178	»
Меркаптотиозолин 11)	0,020	1,8	3,1	1,8	0,101	—
2-фенил-2-меркаптобутиламин 12)	0,066	0,5	0,3	0,6	0,091	Отсут. absent
Сульфиды 13)						
Динзовторичный гептилсульфид 14)	0,05	2,0	2,9	2,3	0,020	1,88
Динзовторичный гептилсульфид 15)	0,10	2,1	3,2	2,7	0,029	1,90
То же	0,15	2,9	4,5	5,3	0,040	2,0
Метилбензилсульфид 16)	0,05	2,0	2,2	2,2	0,020	0,21
»	0,10	2,1	2,6	2,3	0,020	0,82
»	0,15	2,2	3,0	2,3	0,021	1,00
Изогексилфенилсульфид 17)	0,05	2,0	3,3	1,9	0,020	Отсут.
»	0,10	2,7	4,9	2,0	0,030	1,00
»	0,15	3,4	7,0	2,2	0,038	1,10
Бутил вторичный октилсульфид 18)	0,05	2,1	4,5	3,0	0,022	1,10
То же	0,10	3,3	4,9	4,1	0,030	1,15
» »	0,15	4,0	6,6	7,8	0,041	2,10
Дисульфиды 19)						
Дивторичный октилсульфид 20)	0,05	3,1	6,7	3,5	0,035	3,02
То же	0,10	4,0	8,2	5,2	0,050	3,00
» »	0,15	5,2	10,1	5,8	0,070	Отсут. absent
Тиофаны 21)						
α-(2-метиламил) тиофан 22)	0,05	3,0	3,4	2,3	0,021	»
» »	0,10	3,8	3,9	3,1	0,029	»
» »	0,15	5,2	7,2	5,0	0,040	»
α-(3-фенилпропил) тиофан 23)	0,05	2,6	4,3	2,2	0,020	1,12
» »	0,10	3,0	4,8	2,3	0,031	1,15
» »	0,15	3,8	8,3	2,7	0,011	1,13

(see page 8a for key to table 2)

Сернистые соединения 1)	Концентрация сернистых соединений, выраженная в содержании серы в топливе в вес. % 2)	Коррозия в г/м² 3)	Отложения на пластинке в г/м² 4)	Нерастворимые осадки в мг/100 мл 5)	Оптическая плотность после фильтрации 6)	Кислотность мг KOH/100 мл 7)
α-(гексил) тиофан 24)	0,05	3,8	4,3	2,2	0,019	[illegible]
» »	0,10	3,7	3,8	2,5	0,035	0,98
» »	0,15	5,0	5,9	4,0	0,048	Отсут
α-(октил) тиофан 25)	0,05	2,7	3,4	2,2	0,022	»
» »	0,10	3,2	3,7	2,3	0,030	»
» »	0,15	3,1	4,2	2,8	0,048	»
α-(метилбутил) тиофан 26)	0,05	2,3	2,7	2,5	0,029	2,30
» »	0,10	2,6	4,0	2,5	0,043	2,40
» »	0,15	3,0	4,9	2,7	0,060	2,43
Тиофены 27)						
Тиофен 28)	0,05	2,7	4,2	2,0	0,021	2,30
»	0,10	2,6	4,9	2,3	0,030	2,41
»	0,15	2,6	8,6	2,7	0,042	2,52
α-(октил)тиофен 29)	0,05	1,9	10,0	2,1	0,030	Отсут
»	0,10	2,0	9,9	2,5	0,048	1,02
»	0,15	3,2	11,2	2,7	0,062	2,30
Смеси сернистых соединений 30)						
Дибутилдисульфид с диизоамилсульфидом 1:1 31)	0,05	2,6	6,2	2,3	0,027	Отсут
То же	0,15	4,9	8,2	4,1	0,040	1,81
» »	0,25	6,6	10,8	4,7	0,081	[illegible],82
Дибутилдисульфид с диизоамилсульфидом (80%), вторичный октилмеркаптан (20%) 32)	0,05	7,2	25,2	5,2	0,091	0,60
Дибутилдисульфид с диизоамилсульфидом (93,4%), вторичный октилмеркаптан (6,6%) 33)	0,15	10,8	27,6	8,9	0,102	1,22
Естественные сернистые соединения, выделенные из топлив 34)						
Сернистые соединения из ТС-1 35)	0,05	2,4	1,3	[illegible]	0,025	1,81
То же	0,15	3,2	1,7	[illegible]	0,045	1,24
» »	0,25	4,0	8,1	3,5	0,100	0,61
» »	0,21					
Меркаптаны 36)	0,01	15,0	31,6	16,9	0,1[illegible]5	Отсут
Сернистые соединения из топлива ДА	0,05	3,7	6,0	3,5	»	3,02
То же	0,15	3,9	9,3	4,7	»	3,08

Mercaptothiosoline in concentration of 0.02% does not raise the corrosion of bronze and residue formation.

In this way, the properties of mercaptanes depend upon the structure of the radical. Aliphatic mecaptanes sharply intensify the corrosion properties of the fuels and reduce their ttermooxidation stability. Combined presence of thiol, amine and phenyl groups improv the anticorrosion properties.

Addition to the hydropurified fuel TC-1 of 0.05% of individual sulfides, has practically no effect on its corrosiveness and thermal stability. At an increase in the number of sulfides to 0.15% there is observed a noticeable increase in bronze corrosion, tar and residue formation.

Disulfides show a somewhat better effect on the exploitational characteristics of fuels in comparison with sulfides of the very same structure. Thiophanes and thiophenes are little different from sulfiess; the very same rules appear. connected with their structure.

When adding 0.01% of aliphatic mercaptan to fuels, containing 0.04 and 0.14% of aliphatic sulfide and aliphatic disulfide mixture, corrosion of bronze and residue formation rise by 2.2 - 2.8 times, which again confirms the special activity of aliphatic mercaptanes. It should be mentioned, that corrosion processes of bronze, residue and tar formation in fuels change upon the addition of sulfurous compounds in one direction: if metal corrosion is intensified, then the oxidizing condensation processes are intensified simultaneously. The action of fractions which are separated from TC-1 fuel and Diesel fuel DA of natural sulfurous compounds on the properties of jet fuels investigated by us is analogous to the average effect of sulfides, disulfides and thiophenes. Consequently, the properties of synthesized sulfurous compounds from the investigated viewpoint, correspond approximately to properties of sulfurous compounds, contained in fuels.

Conclusions

1. Aliphatic cercaptanes, contained in fuel as a result of long-~~lasting~~ heating ~~of same~~ at 150°, cause sharp corrosion of bronze and formation of tars and insoluble residue. It is necessary to reduce the mercaptan content in fuel.

2. The investigated sulfurous compounds, by their corrosive effect on metals and the effect of tar and residue formation processes in fuels during their heating to 150°, are divided into the following descending series: mercaptanes, disulfides, aliphatic sulfides, aromatic sulfides, thiophanes.

Key to Table 1 -

1) compound: 2) boiling point (in mm of mercury column); 3) molecular weight; 4) content of sulfur in weight, %; 5) mercaptanes; 6) secondary octylmercaptan marcaptothiozolin: 7) 2-phenyl-2-mercaptobtylamine; 8) sulfides; 9) diisoscecondary heptylsulfide; 10) methylbenzylsulfide: 11) Izohexylsulfide; 12) butyl and secondary octylsulfide: 13) disecondary octyl sulfide: 14) thiophanes: 15) -(2-methyl)thiophane; 16) -(3-phenylpropyl) thiophane; 17) -(hexylthiophane: 18) -(octylthiophane; 19) -(2-methylbutyl) thiophane: 20) tiophenes; 21) -octylthiophene; 22) thiophene; 23) sulfurous compounds, separated from fuels; 24) sulfurous compounds, separated from TC-1; 25) sulfurous compounds, separated from DA fuels.

Key to Table 2 -

1)sulfurous compounds; 2) concentration of sulfurous compounds expressed in content of sulfur in fuel in weight %; 3) corrosion in g/m^2; 4)the position on plates in g/m^2; 5) nonsoluble residue in mg/100 ml; 6) optical density after filtration; 7) acidity $\frac{mg\ KOH}{100\ ml}$; 8) basic fuel; 9) mercaptanes; 10) secondary octyl; 11) mercaptothizolin; 12) 2-phenyl-2-mercaptobutylamine; 13) sulfides; 14) diisosecondary heptyl sulfide; 15) diisosdecondary heptyl sulfide; 16) methylbenzylsulfide; 17) Isoexilphenylsulfide; 18) butyl secondary octyl sulfide; 19) disulfides; 20) secondary oxylsulfide: 21) thiophanes:/ 22) -(2-methylamyl) thiphane; 23) -(3-phenylpropyl) thiophane: 24) -(hexyl)thiophane: 25) -(octyl)thiophane; 26))metyulbutyl)thiophane: 27) thiophanes: 28) thiophene: 29) -(octyl) thiophene: 30) mixtures of sulfurous compounds: 31) dibutyldisulfide with diisoamylsulfide 1 : 1; 32) dibutylamylsulfide (80%), secondary octylmercaptan (20%): 33) dobutyldisulfide with diisoamylsulfide (93.4%), secondary octylmercaptan (6.6%); 34) natural sulfurous compounds separated from fuels; 35) sulfurous compounds from TC-1; 36) mercaptanes; 37) sulfurous compounds from DA fuel.