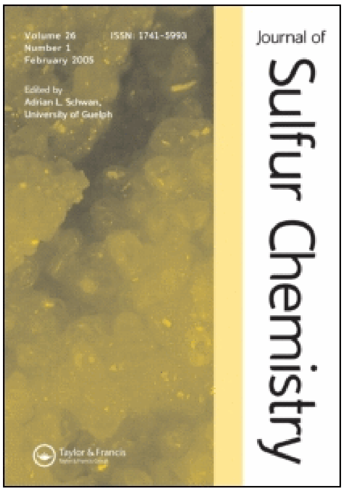

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The Effect of Organic Sulfur Compounds on the Antiwear Properties of Aircraft Fuels

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THE EFFECT OF ORGANIC SULFUR COMPOUNDS ON THE ANTIWEAR PROPERTIES OF AIRCRAFT FUELS

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The antiwear properties of fuels are of great importance in their usage. The aircraft fuel system contains some precision aggregates with a rather small clearance between fuel-lubricated friction parts. With poor lubricating properties of fuels the reliability of the fuel system is diminished which, in turn, decreases the reliability of the flying vehicle.

This problem is complicated by the fact that removal of heteroorganic compounds from fuels in order to increase their thermal-oxidative stability leads to a deterioration of the antiwear properties of the fuels. Due to their higher polarity and lower stability as compared to hydrocarbons, organic sulfur compounds should produce a pronounced effect on the antiwear properties of fuels.

At present it does not seem possible to explain the antiwear effect of some heteroorganic compounds in terms of solely physical phenomena such as adsorption of surfactants at the friction surface. The friction process is most likely to involve physical and chemical interactions of heteroorganic compounds with superficial layers of metal.

The object of this work is to investigate the effect of sulfur compounds on the antiwear properties of jet fuels.

The energy state of the metal surface is known to be related to the imperfection of the crystal structure and the presence of impurities in the metal. The ability of the metal to interact with the environment is determined by the free energy (E) and its variation (ΔE).

The interaction of a fuel with a metal is the result of adsorption processes and chemical reactions. The adsorption leads to a decrease of the free energy of the metal surface (ΔE) and of its entropy (ΔS). The entropy decrease is due to loss of degrees of freedom by the adsorbed layer molecules. The enthalpy of the system, $\Delta H = \Delta E + T\Delta S$, decreases since the adsorption processes are exothermic.

Sulfur compounds and other polar compounds are the first to be adsorbed on the metal surface since they possess higher dipole moments than hydrocarbons (Table 1). In this case ΔH varies to the greatest extent.

At first, chemosorption processes leading to the formation of a monolayer of molecules occur at the metal surface. The structure of this monolayer is greatly affected by the inhomogeneity of the force field at the metal surface. Upon marked variations in the force field potential energy the cavities act as adsorption sites. This localizes the molecular adsorption of polar additives (Fig. 1). This alternation of the microfield polarity

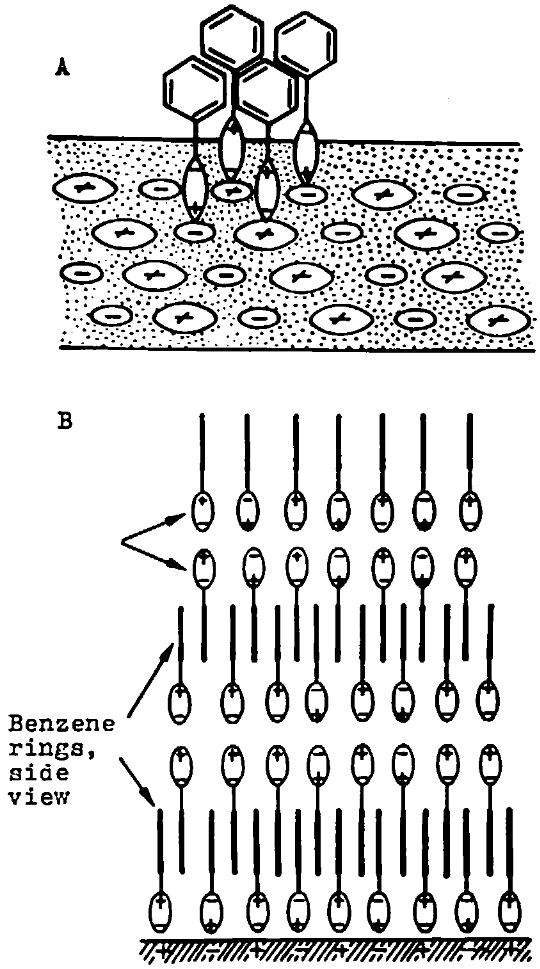


FIGURE 1. The formation of a monolayer (A) and subsequent monolayers (B) of thiophenols at the surface of an energetically inhomogenous metal.

of the crystal lattice of metals is of great importance for the formation of the monomolecular boundary layer. The latter constitutes the basis for further development of a multimolecular layer representing a single system of oriented structures formed under the influence of the surface field force (Fig. 2).

Everything said so far is confirmed by measurements of the boundary layer thickness with variable load in sulfur compound-containing fuels (Table 2) as well as by measurements of the potential contact difference (PCD) between a gold (99.98%, standard) and a steel plate before and after sulfur compound treatment (PCD_1 and PCD_2, respectively). The difference, $\Delta PCD = PCD_2 - PCD_1$ is proportional to the electron escape work (EEW) taken with the opposite sign ($\Delta PCD = -\Delta EEW$). As seen from the above data (Fig. 3), sulfur compounds greatly enhance the PCD and, correspondingly, the antiwear properties of fuels (Table 3).

TABLE I

Dipole Moments of Hydrocarbons and Organic Sulfur Compounds under Normal Conditions[4]

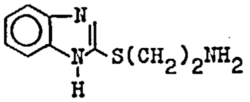
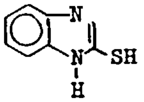
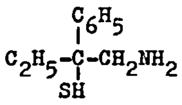
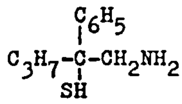
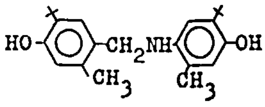
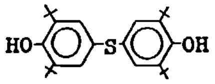
Compounds	Dipole moment, D
Alkanes and cycloalkanes	0
Arenes	0.1–0.9
Thiophenol	1.33
1-Methyl-2-mercaptonaphthalene	1.27
Diphenyl sulfide	1.47
Diphenyl disulfide	1.91
Diallyl sulfide	1.28
2-Propanethiol	1.55
2,5-Dimethylthiophene	0.51
Dibenzothiophene	0.83
Thianthrene	1.7
1,4-Bis-(methylthio)naphthalene	1.93
Phenyl-4-aminophenyl sulfide	2.92
2,3-Diphenyl-2,5-endothio-1,3,4-thiadiazoline	8.8
N-Methylthioacridone	5.2
N,*N*-Phenylethyl-*N*′-allylthiourea	5.1
(*N*,*N*-Diethylamino)-methylbenzothiazolene	4.38

TABLE II

The effect of Organic Sulfur Compounds on the Boundary Layer Thickness (μm) in Contact of Loaded Metals in Fuel Media

Additive	Concentration in fuel, wt. % based on sulfur	Contact pressure mPa		
		0.5	2.5	5.0
1	2	3	4	5
Starting fuel (without heteroorganic compounds	–	0.006	0.004	0.003
Thiophenol	0.0500	0.08	0.07	0.06
	0.0250	0.07	0.06	0.05
	0.0125	0.06	0.05	0.04
2-Octanethiol	0.0550	0.04	0.03	0.02
	0.0250	0.03	0.02	0.01
	0.0125	0.02	0.01	0.009
1-Methyl-2-mercaptonaphthalene	0.0500	0.09	0.08	0.07
	0.0250	0.08	0.07	0.06
	0.0125	0.07	0.06	0.05
Diphenyl sulfide	0.0500	0.08	0.07	0.06
	0.0250	0.07	0.06	0.05
	0.0125	0.06	0.05	0.04
Diallyl sulfide	0.0250	0.03	0.02	0.01
	0.0250	0.02	0.01	0.007
	0.0125	0.01	0.007	0.005

TABLE II (Continued)

Additive	Concentration in fuel, wt. % based on sulfur	Contact pressure mPa		
		0.5	2.5	5.0
1	2	3	4	5
Diphenyl disulfide	0.0500	0.08	0.07	0.06
	0.0250	0.07	0.06	0.05
	0.0125	0.06	0.05	0.04
Dioctyl disulfide	0.0500	0.04	0.03	0.02
	0.0250	0.03	0.02	0.01
	0.0125	0.02	0.01	0.008
2,5-Diethylthiophane	0.0500	0.06	0.05	0.04
	0.0250	0.05	0.04	0.03
	0.0125	0.04	0.03	0.02
2,5-Diethylthiophene	0.0500	0.03	0.02	0.01
	0.0250	0.02	0.01	0.006
	0.0125	0.01	0.008	0.004
Dibenzothiophene	0.0500	0.07	0.06	0.05
	0.0250	0.06	0.05	0.04
	0.0125	0.05	0.04	0.03
2-Ethylbenzothiophene	0.0500	0.06	0.05	0.04
	0.0250	0.05	0.04	0.03
	0.0125	0.04	0.03	0.02
	0.05	0.08	0.06	0.04
	0.025	0.07	0.06	0.04
	0.0125	0.07	0.05	0.03
	0.02	0.06	0.04	0.03
	0.015	0.06	0.04	0.03
 $C_2H_5-\underset{SH}{\overset{C_6H_5}{C}}-CH_2NH_2$	0.05	0.05	0.03	0.02
 $C_3H_7-\underset{SH}{\overset{C_6H_5}{C}}-CH_2NH_2$	0.05	0.06	0.04	0.03
	0.05	0.08	0.07	0.03
	0.050	0.09	0.07	0.04
	0.025	0.08	0.07	0.04
	0.0125	0.07	0.05	0.03
PMA M-2	0.050	0.009	0.008	0.002

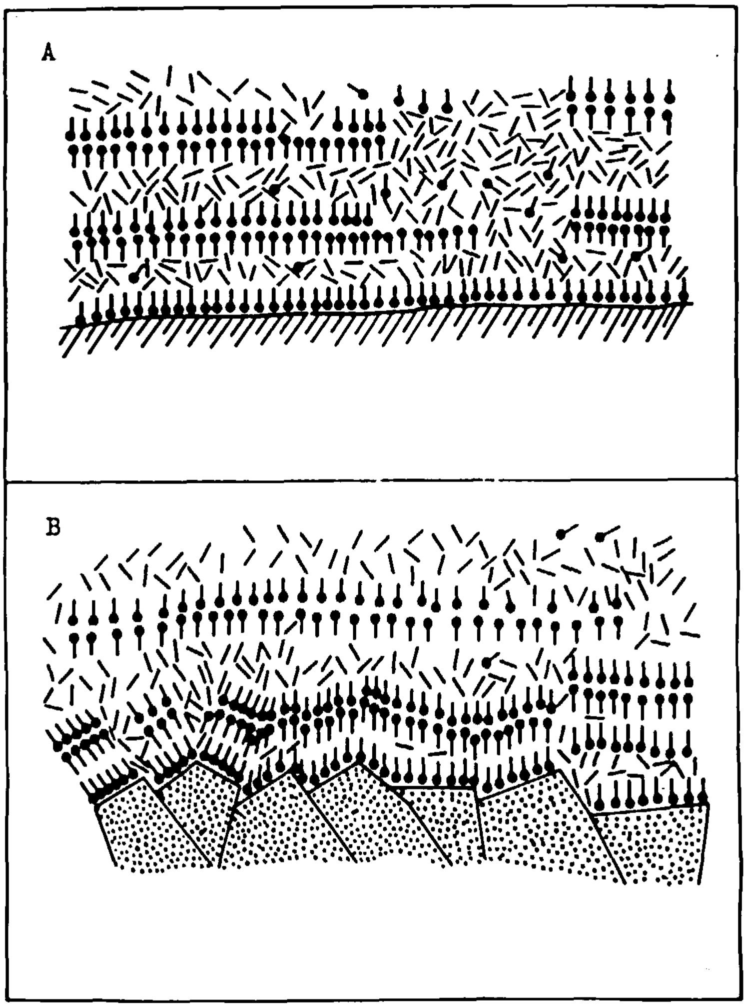


FIGURE 2. Model of the boundary layer of organic sulfur compounds in hydrocarbons on a polished homogenous (A) and an unpolished heterogenous metal (B).

The effect of sulfur compounds on the antiwear properties of the fuel T-7 has been studied on a specially constructed unit modelling the usage of fuel as a lubricating-medium in modern aircraft engines. A friction pair comprises regulating pump plungers of HVG steel and an accessory plate of bronze or AMG alloy. The tests were carried out at 100 °C and a sliding speed in the friction zone of 1.8 m/sec. The antiwear property index (AWI) was used as a criterion of estimation:

$$\text{AWI} = \Delta G(I + L_t/360)\ \text{mg}$$

where ΔG is the wear-induced change of the plate weight in mg; L_t is the length of the circular wear trail, occupied by deformational shifts of metal in mg.

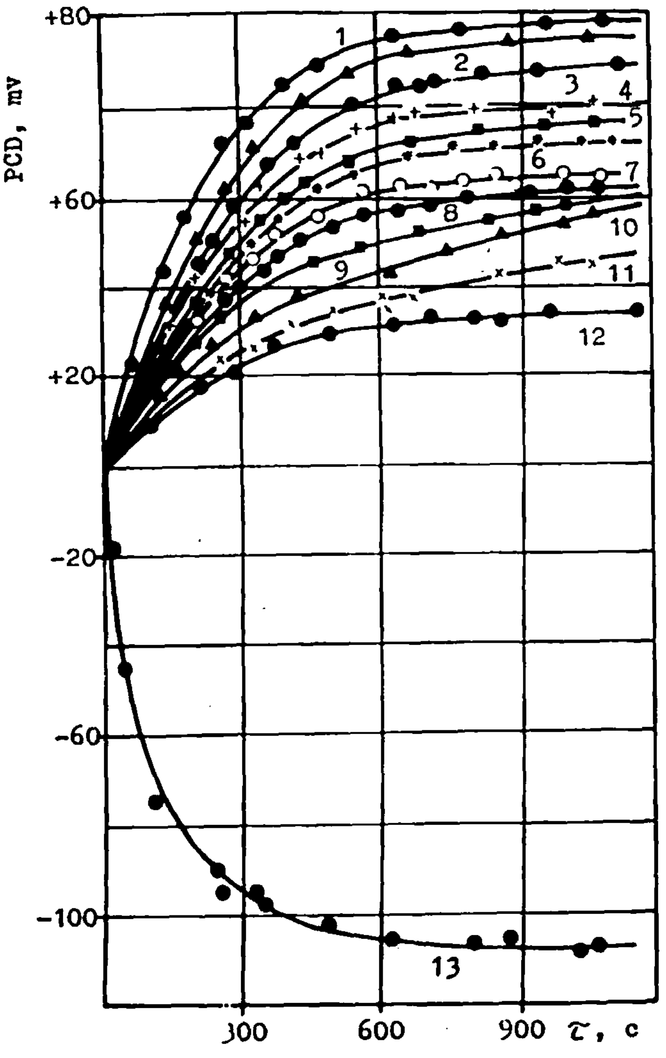


FIGURE 3. The effect of organic sulfur compounds on the potential contact difference (PCD): 1. 2-mercaptobenzothiazole; 2. 2-mercaptobenzimidazole; 3. 2-(2-amidodimethylene)thiobenzimidazole; 4. 1-amino-2-mercapto-2-phenylpentane; 5. thiophenol; 6. 1-methyl-2-mercaptonaphthalene; 7. diphenyl disulfide; 8. diphenyl sulfide; 9. dioctyl disulfide; 10. 2,5-diethylthiophane; 11. 2,5-diethylthiophene; 12. 2-ethylbenzothiophene; 13. fuel T-7 highly refined from heteroorganic compounds.

The formation of oriented layers is the first stage towards subsequent transformations of sulfur compounds and hydrocarbons upon metal friction in a fuel medium. Sulfur compounds and their transformation products interact with superficial layers of metal changing their structure, composition, and properties and thus affecting the structural mechanism of plastic deformation upon friction.

TABLE III

The Effect of Organic Sulfur Compounds on the Antiwear Properties (mg) of the Fuel T-7 (Average Data for Three Measurements)

		AWI at sulfur compound concentrations, wt. % based on sulfur							
Compounds	Materials	0	0.001	0.005	0.010	0.030	0.06	0.100	0.140
1	2	3	4	5	6	7	8	9	10
Thiophenol	AMG-5M	2.6	2.75	1.30	1.35	1.20	1.85	2.00	2.32
	Bronze	23.5	22.00	19.00	2.00	1.65	1.80	2.30	2.78
2-Octanethiol	AMG-10	2.6	3.20	1.70	1.10	1.75	1.75	1.95	2.38
	Bronze	23.5	20.80	10.80	11.50	8.80	10.40	10.20	12.42
1-Methyl-2-mercapto-naphthalene	AMG-10	2.6	2.72	1.22	1.30	1.22	1.83	1.94	2.48
	Bronze	23.5	20.08	17.08	1.82	1.48	1.62	1.94	2.58
Diphenyl sulfide	AMG-10	2.6	2.83	1.48	1.38	1.23	1.38	1.49	2.48
	Bronze	23.5	23.07	18.42	2.04	1.82	1.78	1.92	2.59
Diallyl sulfide	AMG-10	2.6	2.84	2.09	1.42	1.39	1.28	3.42	4.28
	Bronze	23.5	21.92	19.42	2.62	2.58	2.42	3.28	4.07
Diphenyl disulfide	AMG-10	2.6	2.93	2.48	2.32	1.92	1.42	1.83	3.98
	Bronze	23.5	23.9	20.81	8.4	7.42	4.3	3.8	4.87
Dioctyl disulfide	AMG-10	2.6	2.86	3.08	2.91	2.72	2.43	2.20	3.88
	Bronze	23.5	23.57	18.41	9.21	4.32	2.38	2.42	4.37
2,5-Diethylthiophane	AMG-10	2.6	2.93	3.42	3.34	2.98	2.68	2.42	2.87
	Bronze	23.5	24.2	22.41	15.3	7.4	2.98	2.43	3.92
2,5-Diethylthiophene	AMG-10	2.6	2.72	2.68	2.44	2.12	2.08	1.93	3.42
	Bronze	23.5	23.7	22.42	20.41	16.40	8.39	4.81	6.46
Dibenzothiophene	AMG-10	2.6	2.76	2.46	2.40	2.38	2.36	2.31	3.44
	Bronze	23.6	23.9	20.01	17.40	11.18	7.32	3.84	4.35
2-Ethylbenzothiophene	AMG-10	2.6	2.84	2.52	2.44	2.38	2.28	2.22	4.18
	Bronze	23.6	24.05	23.00	16.3	10.09	7.32	4.08	6.30

Mercaptans considerably improve the antiwear properties of the fuel T-7. These properties deteriorate only at mercaptan concentrations above 0.06% (Table 3). With other additives the antiwear properties are also improved; however, the efficiency of additives decreases in the order mercaptans > disulfides > sulfides > t-hiophanes > thiophenes. In all cases some optimal sulfur compound concentrations for the improvement of the fuel antiwear properties have been found. This minimum slowly shifts towards higher concentrations in the above series.

It should be noted that at lower mercaptan concentrations the fuel AWI in steel/aluminium friction decreased. This phenomenon requires further investigation.

The high antiwear efficiency of sulfur compounds with identical functional groups, but different hydrocarbon moieties indicates the essential role of the hydrocarbon framework being more important than that of the sulfur-containing functional group. The hydrocarbon skeleton shifts the optimal concentration in each sulfur compound class.

Wear products isolated from fuel by ultracentrifugation, followed by isopentane washing of the hydrocarbon phase have been studied by IR spectroscopy and X-ray diffraction. The IR spectra of wear products depend on the structure of the sulfur compounds on the metals under friction.

An analysis of the spectra allows some general regularities to be recognized.

1. Moderately intense absorption of C–H bonds characterizing the organic portion of the wear products, predominantly saturated ones (2960, 2920, 2870, 1460, 1380 cm^{-1}), but sometimes aromatic (in low quantities, 3100 cm^{-1}); C=O group absorption (1720 cm^{-1}); more or less distinct absorption at 1200 cm^{-1}, partly due to C–O and O–H bonds and, more probably, S=O bonds (HSO_4^-, SO_4^{2-}). All the spectra display also an adsorption of highly diverse intensity in the region 1400–1420 cm^{-1}, open to ambiguous interpretation. The absorption complex 1720–1420–750 cm^{-1} and the absorption region 3600–29000 cm^{-1} provide evidence for the possible presence of free organic acids in the containing aromatic sulfur compounds due to steel/bronze friction. The reaction of the products of fuel oxidation with metals leads to secondary products; the absoprtion band complex 1570–1600, 1420 cm^{-1} can be attributed to the presence of organic acid salts. It should be noted that the possible presence of salts is more definitely expressed with

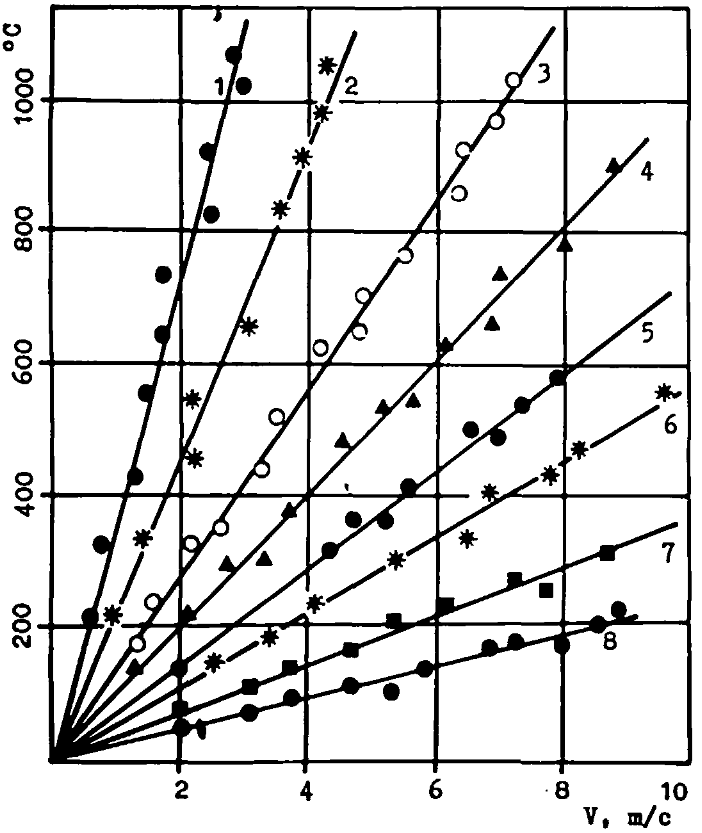
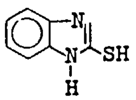
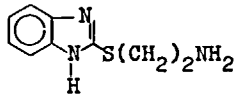
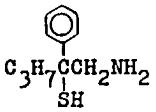
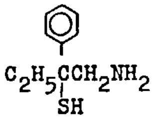
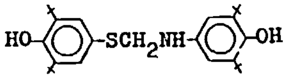
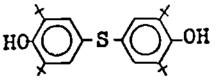


FIGURE 4. The effect of the sliding speed, V, on the temnperature in the constantane/steel friction zone under a pressure of 5 mPa. 1 — without lubrication; 2 — highly refined fuel T-7; 3 — heavier highly refined hydrocarbon fuel (190–270 °C); fuel T-7 with additives (wt. % based on sulfur) of dioctyl sulfide (4), diphenyl disulfide (5), thiophenol (6), 2-mercaptobenzothiazole (7), 2-mercaptobenzimidazole (8).

TABLE IV

The Effect of Additives on the Antiwear Properties of the Fuel T-7 at 100 °C[5]

Additives	Concentration, wt. %	AWI, mg	Concentration, wt. % based on sulfur	AWI, mg
Starting fuel	–	23.5	–	23.5
	0.020 0.015	3.6 3.8	0.03	0.95
	0.0500 0.0250 0.0125	3.2 4.3 4.8	0.03	0.98
	0.050	3.4	0.03	1.07
	0.05	4.8	0.03	1.12
	0.0500 0.0250 0.0125	1.80 1.98 2.38	0.04	0.78
	0.0500 0.0250 0.0125	4.3 4.2 4.0	0.04	0.82
$H_{37}C_{18}NHC_3H_7$	0.050	11.4	0.05*	6.3

* based on nitrogen

the pair steel/bronze (the relative intensity of absorption is higher in the region 1570 and 1420 cm^{-1}).[1]

2. A prominent effect of the structure of sulfur compound additives on the composition of the wear products which shows a direct participation of the sulfur compounds in the formation of the latter. This is especially clearly defined with the friction pair steel-bronze.

The spectra of the wear products formed in the presence of thiophene, diphenyl sulfide, and diphenyl disulfide are in many respects analogous to the corresponding sulfur compound spectrum. For instance, the absorptions at 700, 740, 940, 1000, 1040 and those in the region 1100, 1200, 1400–1500 cm^{-1}, corresponding mainly to the organic part. The SH group (with a sharp intense band at 2590–2550 cm^{-1}) is not present in the spectrum of the wear products, thus indicating a possible oxidation of this group. This is evidenced by an absorption at 1100–1200 cm^{-1}, corresponding to S=O groups. Other sulfur compounds are also oxidized intensively at the sulfur atom to produce S=O, SO_2, and SO_3H groups. In the case of thiophenes no SO_3H groups are formed.

3. A considerable intensity of absorption bands at 1200, 1400, and 1600 cm^{-1}, inconsistent with the absorption intensity of bonds in organic molecules, which indicates a possible predominance in the wear products of inorganic components, i.e., various sulfates (HSO_4^- 1180–1160, 1080–1000, 880–840 cm^{-1}, 880–800 cm^{-1}).

The X-ray diffraction patterns of the steel-bronze friction products show the presence of a crystalline phase of copper sulfides in all the samples. There are also particles of bronze and aluminum-magnesium alloys in the samples.

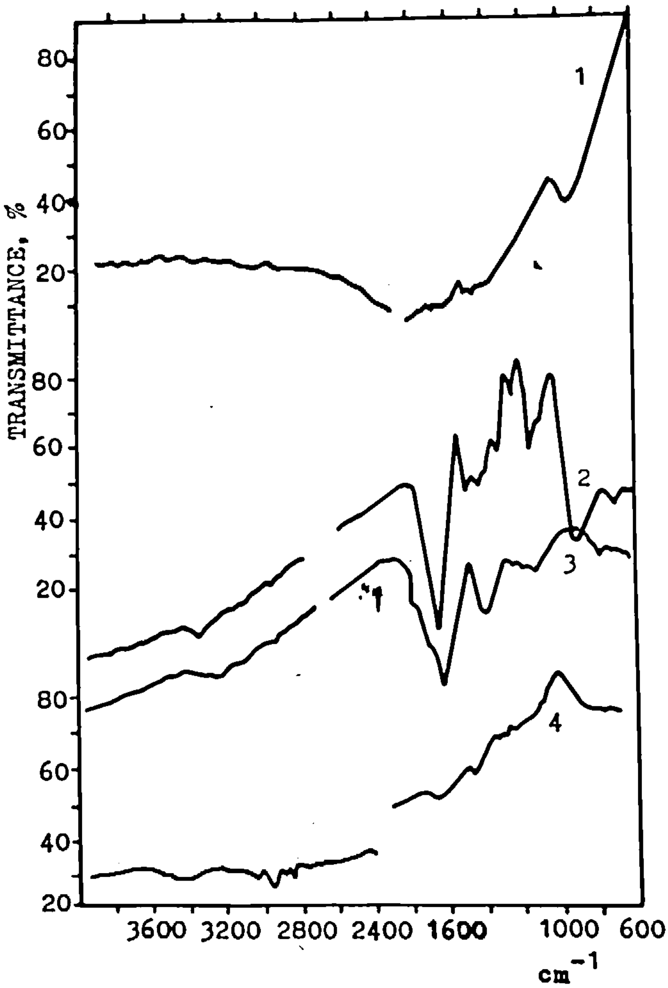


FIGURE 5. IR spectra of wear products. 1 — initial fuel T-7; fuel T-7 + 0.025% 2-(2-aminodimethylylenethio)benzimidazole (2), diphenyl sulfide (3), isopropyloctadecylamine (4).

Upon friction of precision pairs of jet fuel system aggregates the temperature of the rubbing surfaces increases. Sulfur compounds, when introduced into the fuel, considerably decrease the temperature of the rubbing parts (Fig. 4). During supersonic flights this temperature is further increased by fuel heating due to aerodynamic and other factors.[2]

The use of specially synthesized sulfur-containing additives could greatly improve the antiwear properties of fuels. Apart from sulfur, the synthetic additives may also contain nitrogen and oxygen and sometimes phosphorus and chlorine. The antiwear additives should also act as antioxidants and dispersants. Such additives have already been produced (Table 4). At elevated temperatures the adsorbed layers of additives undergo thermal and thermal-oxidative transformations. For a better plastification of the metal boundary layers an optimal stability of the compounds absorbed is required. Similar to the sulfur compound oxidation, the sulfur-containing additives are oxidized first to S=O and SO_2 compounds and decompose at the S–C and N–C bonds. The IR spectra of the wear products formed in the friction zone clearly indicate the presence of sulfates and sulfites (1120–1180 cm^{-1}). Weak bands near 3400 cm^{-1} show the presence of a negligible amount of OH groups.

The IR spectra and X-ray patterns of the wear products in the friction zone provide evidence for the presence of hydroxides (870, 1130, 1170, 1410, 1530 cm^{-1}) and oxides (870–830 cm^{-1}) of metals in contact by friction. There are also metal sulfides among the wear products. This structural degradation of the additives in the boundary layer goes so far that the organic part of the wear products is poorly manifested (Fig. 5).

Heteroatoms, sulfur first of all, are very essential in the formation of low melting eutectics and plastified layers. Sulfur is found in the boundary layer of the metal at a depth of 25–30 μm.[2,3]

In contrast, the metal wear products in fuels highly purified with regard to heteroorganic compounds mainly consist of metal oxides ($\sim$900 cm^{-1}) and, to a considerably lower extent, of metal hydrates. The organic part is poorly expressed in the IR spectra of the wear products.

Thus the addition of natural and synthetic sulfur compounds to highly refined hydrocarbon fuels may considerably improve the antiwear properites of the latter.

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