References [1-3] show that the use of jet fuels at higher temperatures leads to formation of a solid phase, which makes them difficult to filter. It has been established [1, 2, 4] that organosulfur compounds have marked effects on the formation of the solid phase.

The present paper deals with the effect of the structure of organosulfur compounds on the composition and structure of the solid phase formed during oxidation of the hydrocarbons of jet fuels.

The investigation was performed on n-nonyl mercaptan, phenyl mercaptan, dioctyl disulfide, diphenyl disulfide, dioctyl sulfide, and α-hexylthiophane of purities 99.0-99.2%. The organosulfur compounds (0.2% in terms of sulfur) were added to TS-1G fuel, which was subjected to adsorption treatment to remove small admixtures of heteroorganic compounds.

The TS-1G fuel had the following physicochemical properties: boiling range 141–242°C, crystallization temperature –68°C, and viscosity at 20°C 1.29 cs. It contained 29.1% of normal alkanes, 29.3% of isoalkanes and alkyl derivatives of cyclopentane, 18.6% of homologs of cyclohexane, 1.8% of decalin, 16.4% of monocyclic aromatic hydrocarbons, 3.9% of condensed aromatic hydrocarbons, and 0.09% of unsaturated hydrocarbons. About 8% of the aromatic hydrocarbons had cyclic-aromatic structures.

Mixtures of TS-1G fuel and individual sulfur compounds were studied by methods developed in [4, 5]. We also studied the absorption kinetics of oxygen at 150°C and the composition of the oxidation products. The precipitate formed during oxidation was separated from the fuel, washed thoroughly with isopentane, and dried to constant weight at 50–60°C. The precipitate was then studied by instrumental and chemical analysis methods.

Analysis of the soluble oxidation products [6], and the decrease in the oxygen consumption for the reaction (Fig. 1) indicate that these organosulfur compounds actively retarded oxidation, but a solid phase was formed.

Formation of the solid-phase particles was studied by light dispersion in a specially designed apparatus [6, 10]. It was established that owing to the market tendency of aromatic structures to association and oriented polarizability, thiophenol, diphenyl disulfide, and diphenyl sulfide very actively assist formation and coagulation of solid-phase particles.

The infrared spectra* of the precipitates (Fig. 2) formed during oxidation of TS-1G with individual organosulfur compounds reveal that the main components of the solid phase are sulfur and organosulfur compounds.

The infrared spectra contained bands at 1200, 1130–1140, 1050–1060, and 630 cm⁻¹, due to vibrations of the sulfur-oxygen bond in sulfides, sulfonic acids and their salts, sulfates, covalent sulfonates, and sulfates [7, 8].

The structure of organosulfur compounds has a marked effect on the amount of solid phase formed, and on the structure and composition of the precipitate.

The spectra of the precipitates formed in the presence of aliphatic organosulfur compounds are mutually very similar. The spectra clearly exhibit absorption of the --S-- groups in the esters of sulfinic acids (1130 cm⁻¹), covalent sulfonates and sulfates (1330–1420, 1145–1200 cm⁻¹), ionized sulfonates (1150–1260, 1010–1080, 600–700 cm⁻¹). Sulfones are absent in the precipitates, because no absorption is observed at 1300–1350 cm⁻¹.

*The infrared spectra of the precipitates were recorded in a UR-20 apparatus on specimens tableted from KBr.
Fig. 1. Effects of individual organosulfur compounds on oxidation and formation of a solid phase in TS-1G fuel with additives: 1) diphenyl disulfide; 2) diphenyl sulfide; 3) thiophenol; 4) dioctyl disulfide; 5) n-nonyl mercaptan; 6) α-hexylthiophane; 7) TS-1G fuel. A) Heating to 150°C at 1°C/min; B) oxidation at 150°C; C) cooling to 25°C.

The symmetric and asymmetric vibrations of the C=O group in the carboxyl structure at 1600 and 1420 cm\(^{-1}\) indicate the presence of ionized carboxyl RCOO\(^-\), i.e., salts of carboxylic acids, in the precipitates. The intense absorption at 3450 cm\(^{-1}\) indicates the presence of a hydroxyl group in the precipitates.

The infrared spectra of the precipitates have bands due to the C-H bonds in the CH\(_2\) and CH\(_3\) groups (2960, 2920, 2850, 1460, and 1390 cm\(^{-1}\)), including CH\(_2\) groups in chains with more than four members (720 cm\(^{-1}\)). This is a clear indication that the aliphatic structure of the organosulfur compounds participate in formation of the solid phase.

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The infrared spectra are very similar to that of CuSO\(_4\)·5H\(_2\)O as regards the form and position of the main bands [9].

The spectra of the precipitates formed by oxidation of TS-1G with aromatic organosulfur compounds (see Fig. 2) are mutually very similar, but differ markedly from those described above. The spectra have bands relating to the structure of a monosubstituted aromatic ring: 470, 692, 745, 1025 (1072), 1440, 1480, 1580, 3080 cm\(^{-1}\).

The organosulfur compounds undergo specific structural thermooxidative conversions owing to participation in the formation of the solid phase. This is indicated, in particular, by the absence of bands at 1300 and 1080 cm\(^{-1}\) (these bands are present in the spectra of thiophenol, diphenyl sulfide, diphenyl disulfide) and by the appearance of intense absorption at 1200, 1130, and 630 cm\(^{-1}\) and a weak band at 1040 cm\(^{-1}\); this indicates the formation of sulfoxides, covalent sulfonates, and sulfonic acids and their salts.

Formation of sulfonates, sulfonic acids, disulfides, and thiophanes with TS-1G is accompanied by splitting of the C–S bond.

The solid phase contains oxygen-bearing functional groups –OH and C=O (3400, 1700 cm\(^{-1}\)) – the absorption intensity of which is fairly high.