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### The Effect of Organic Sulfur Compounds on Oxidation Processes of Hydrocarbon Fuels

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# THE EFFECT OF ORGANIC SULFUR COMPOUNDS ON OXIDATION PROCESSES OF HYDROCARBON FUELS

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*(Received 20 April 1987)*

The effect of the structure of organic sulfur compounds on the oxidation processes of individual hydrocarbons and commercial jet and diesel fuels has been studied. The inhibiting properties of sulfur compounds become manifest at low optimum concentrations; at higher concentrations a considerable increase in the oxidation rate is observed and formation of insoluble oxidation products such as gums and sediments occurs. When the structure of organic sulfur compounds is close to that of the hydrocarbon medium, minimum amounts of insoluble oxidation products are formed.

*Key words:* Disulfides, thiols, thiophanes, thiophenes, sulfides, sulfonic acids, sulfinic acids, the inhibition coefficient.

Organic sulfur compounds occur in all petroleum hydrocarbon fuels. With rising boiling point the concentration of sulfur compounds in petroleum fractions increases.<sup>1</sup>

Experimental results obtained in the study of the effect of sulfur compounds on the oxidation processes of jet (TS-1)<sup>†</sup> and diesel (DZ)<sup>§</sup> fuels are reported.

Individual and native sulfur compounds isolated from Samotlor crude (West Siberia) as well as individual hydrocarbons and commercial jet and diesel fuels freed from sulfur compounds have been studied (Tables 1, 2). The purity of the individual sulfur compounds studied was 99.92–99.95 wt. %.

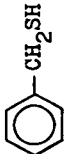
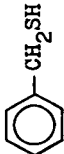
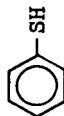

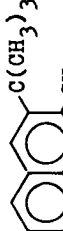
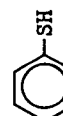
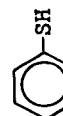

All sulfur compounds inhibit the oxidation of hydrocarbons and mixtures thereof. A significant decrease is observed in the rate of reaction of initiated cumene oxidation carried out at 65 °C in the presence of sulfur compounds (Fig. 1). The induction period increases and the uptake of oxygen decreases (Figs. 2–4). The observed inhibition of the oxidation process can probably be accounted for by the readily proceeding termination of the oxidation chains. The radicals formed from the inhibitors are unreactive and hence they are not involved in the subsequent reactions of chain elongation, recombination occurring among the radicals themselves as well as between the radicals on the one hand and the active chain centres on the other. The inhibition coefficient is 1–2, which is equal to the number of oxidation chains broken by one inhibiting group.

The mechanism of oxidation rate inhibition can be suggested based on the analysis of the variation of the oxidation rate  $W$  versus the initiation rate  $W_i$ . For the oxidation of

<sup>†</sup>TS-1 fuel is used for jet passenger aircrafts.

<sup>§</sup>DZ fuel is used for diesel high-speed engines in winter.

Table 1. Characteristics of the organic sulfur compounds studied

N	Sulfur compound	Structure	Density at 20 °C, kg/m <sup>3</sup>	Molecular mass	Refractive index, n <sub>D</sub> <sup>20</sup>	Boiling point, °C/mm Hg	Melting point, °C
1	1-Nonanethiol	$n\text{-C}_9\text{H}_{19}\text{SH}$ 	843.8	160.325	1.4560	208.2/760	-69.0
2	Phenylmethanethiol		1054.4	124.207	1.5757	195.0/760	-30.0
3	Thiophenol		1076.6	110.180	1.5893	168.7/71	-14.8
4	1-Naphthalenethiol		1160.7	160.240	1.6802	142.3/7 86.5/0.28	83.4
5	3- <i>t</i> -Butyl-2-naphthalenethiol		1023.8	216.348	1.6211	-	-
6	2-Ethylthiophenol		1034.9	138.234	1.5700	210/760	8
7	2-Methylthiophenol		1041	124.207	1.5742	194.2/760	15
8	1-Mercapto-2-hydroxy-4- <i>t</i> -butylbenzene		1079.5	182.286	1.5632	353/0.04	-

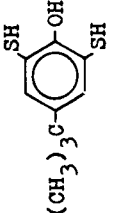
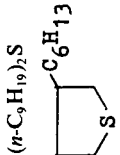

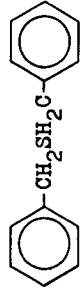
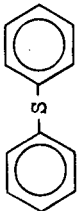
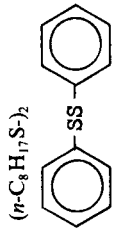
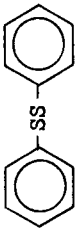

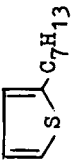
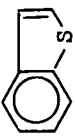
9	1,3-Dimercapto-2-hydroxy-4- <i>t</i> -butylbenzene		214.350	—	417/0.05	—
10	Di- <i>n</i> -nonyl sulfide	$(n\text{-C}_9\text{H}_{19})_2\text{S}$ 	845.5	1.4640	185/5 199/10	—
11	3- <i>n</i> -Hexylthiophane		909.5	1.4823	240/760	—
12	Dibenzyl sulfide		214.332	—	—	48.5
13	Diphenyl sulfide		1110.0	1.6312	162.5/18	—
14	Di- <i>n</i> -octyl disulfide	$(n\text{-C}_8\text{H}_{17}\text{S})_2$ 	290.580	1.4820	199/10	—
15	Diphenyl disulfide		218.344	—	125-137/0.25	61.0
16	Dibenzyl disulfide		246.398	—	—	70.0
17	2- <i>n</i> -Heptylthiophene		926.9	1.5307	144/10 81.5/0.3	—
18	Benzothiophene		1193.7	1.6302	217/760	31.3

Table 1. (cont.)

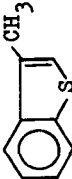
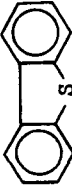

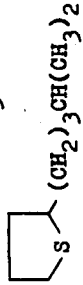
N	Sulfur compound	Structure	Density at 20°C, kg/m <sup>3</sup>	Molecular mass	Refractive index, n <sub>D</sub> <sup>20</sup>	Boiling point, °C/mm Hg	Melting point, °C
19	3-Methylbenzothiophene		at 40°C 1129	148.229	at 40°C 1.6230	128/25	-
20	Dibenzothiophene		-	184.262	-	153/3	99.6
21	Sulfur compounds isolated from TS-1 fuel	$C_{13.2}H_{26.1}S_{1.07}$	938.4	218.74	1.5243	(229-263)/ 760	-13.4
22	Sulfur compounds isolated from DZ fuel	$C_{15.7}H_{29.2}S_{1.11}$	969.8	253.12	1.5328	(242-281)/ 760	-22.7
23	1,3-Dimethylbutylphenyl sulfide	$(CH_3)_2CHCH_2CHSC_6H_5$ 	951.0	194.342	1.5245	123/15	virtification
24	2-(4-Methylpentyl)thiophane		905.0	172.336	1.4798	(88.5-89.5)/ 5	-

Table 2. Characteristics of the hydrocarbons and fuels studied

Hydrocarbons and fuels	Density, $\text{kg/m}^3$ , $^{20}$	Mol. mass	Formula	B.p./b.r., $^{\circ}\text{C}/\text{mm Hg}$	Freezing point, $^{\circ}\text{C}$	Refractive index, $n_D^{20}$	Hydrocarbon composition		
							Alkyl-arenes	Alkylcycloalkanes	Alkanes
<i>n</i> -Hexadecane	774.3	226	$\text{C}_{16}\text{H}_{34}$	286.8/760	+18.2	1.43453	-	-	100
<i>n</i> -Dodecylcyclohexane	825.0	252	$\text{C}_{18}\text{H}_{36}$	132.5/0.8	+12.6	1.4580	-	100	-
<i>n</i> -Propyldecalin (mixture of <i>cis</i> - and <i>trans</i> -isomers)	874.7	180	$\text{C}_{13}\text{H}_{24}$	104/12	-	1.4745	-	100	-
Fuel TS-1*	779.3	140.2	$\text{C}_{10.2}\text{H}_{18.1}$	(148-243)/760	-62.4	1.4351	18.5	20.0	59.5
Alkanes + cycloalkanes isolated from TS-1 fuel	756.9	141.0	$\text{C}_{10.8}\text{H}_{21.6}$	(133-240)/760	-55.3	1.4235	-	100	-
Fuel DZ	858.4	188.9	$\text{C}_{13.9}\text{H}_{22.7}$	(195-335)/760	-48.8	1.4887	20.8	58.2	20.3
Cumene	861.7	120	$\text{C}_9\text{H}_{12}$	152.4/760	-96.0	1.49145	100	-	-

\* The sulfur compounds were carefully removed from the fuels by hydrofining and by additional adsorption refining. The residual sulfur content constitutes 0.0002-0.0004 wt. %. The sulfur contents in the initial fuels DZ and TS-1 were 0.198 and 0.248 wt. %, respectively.

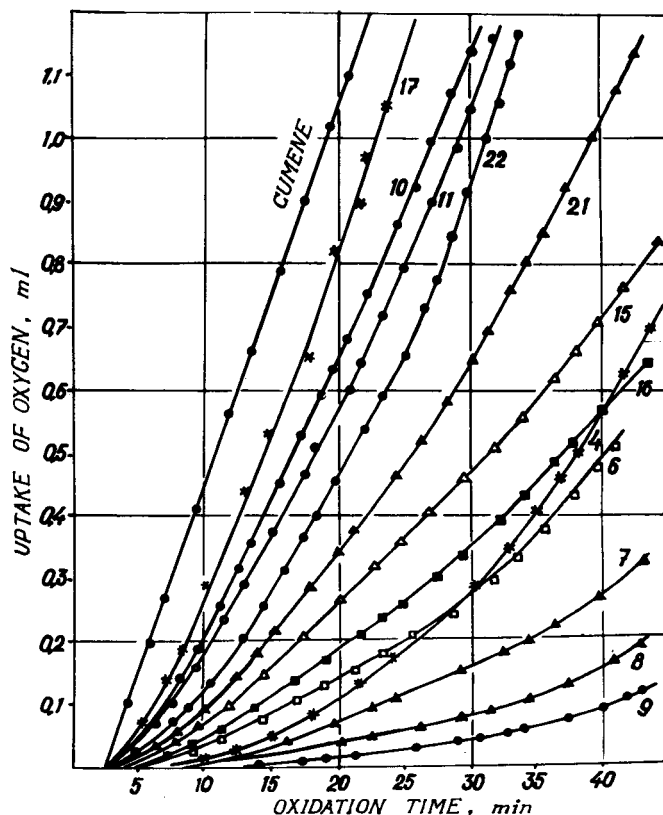


Figure 1 The effect of sulfur compounds (0.01 wt. %) on initiated cumene oxidation. The curve numbers correspond to those used in Table 1.

pure hydrocarbons and mixtures thereof and for second-order chain terminations the following equations hold:

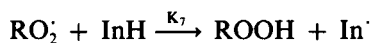
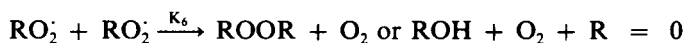
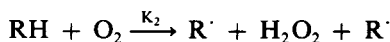
$$W = K_2 \sqrt{(W_i/K_6)} [RH]$$

$$W = W_i^{0.5} K_2 K_6^{-0.5} [RH]$$

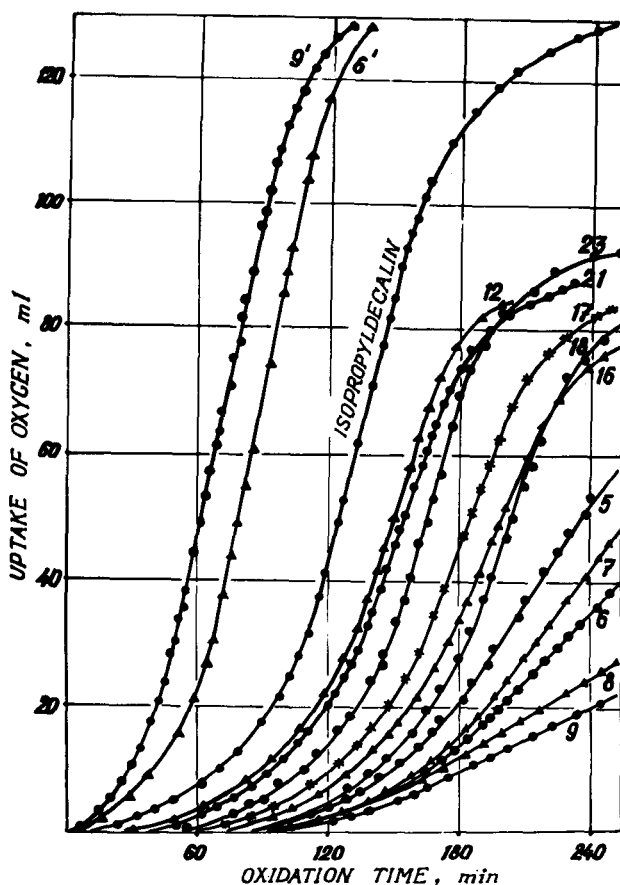
In the presence of an inhibitor and in the absence of second-order chain termination,

$$W = W_i K_2 [RH] / (f K_7 [InH])$$

where  $K_2$ ,  $K_6$  and  $K_7$  are the constants determining the reaction rates:



$f$  is the inhibition coefficient determining the number of radicals subject to termination



**Figure 2** The effect of sulfur compounds (0.01 wt. %) on noninitiated isopropyldecalin oxidation at 150°C. 6', 9': the sulfur compound concentration constitutes 0.3 wt. % (as recalculated for sulfur).

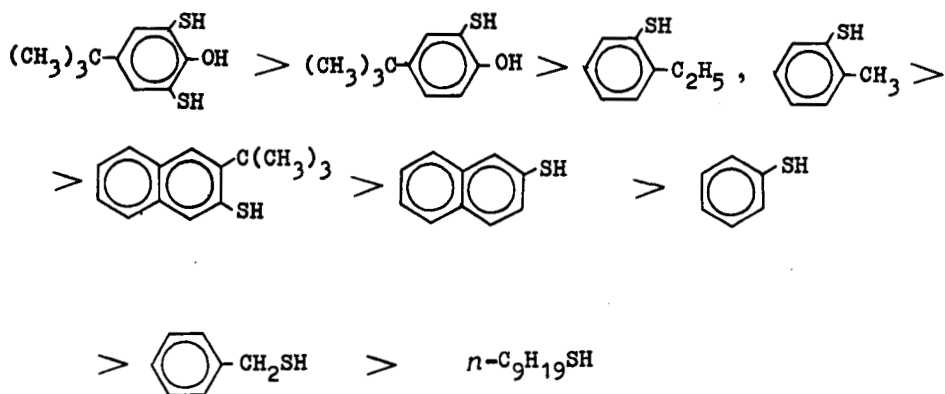
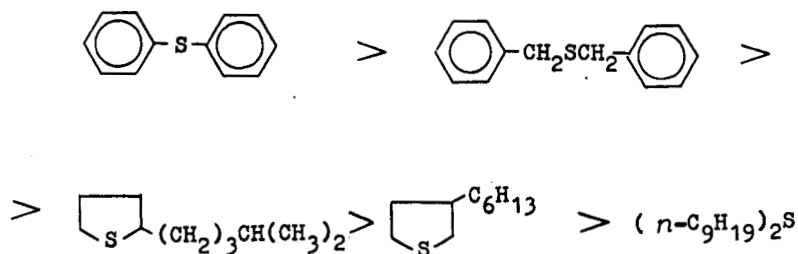
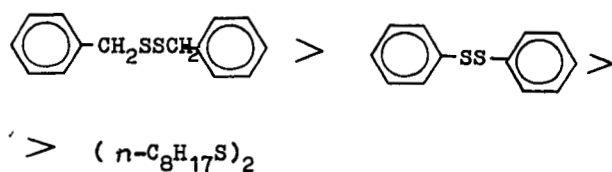
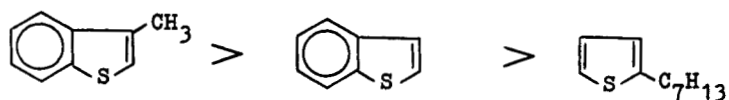
on a single inhibitor molecule and characterizing the inhibition time of oxidation;  $K_7$  is the rate constant of the interaction occurring between the peroxide radicals and the inhibitor; it characterizes the inhibition rate of oxidation.

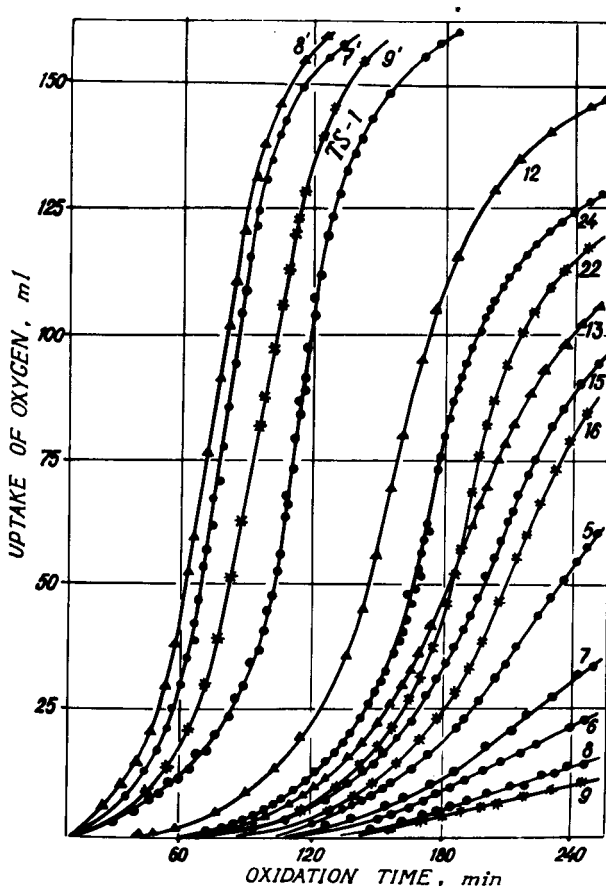
Thus, the inhibition activity increases with  $f$ ,  $K_7$  and  $[InH]$ .

The structure of the sulfur compounds affects their inhibition rates (Figs. 1-4). The order of sulfur compounds studied with respect to their inhibition efficiency is as follows: thiophenes < sulfides < disulfides < thiols<sup>1</sup>. A detailed study made on the inhibition efficiency of sulfur compounds of each class relative to their structure permits to arrange these sulfur compounds in the following order of increasing inhibition efficiency (Table 3, Figs. 2-4). It should be noted that these data were obtained for sulfur compounds of each class, the molar concentration of the functional group (as recalculated for sulfur) being similar in the hydrocarbons. The mass concentration of the sulfur compound is different (Table 1).

The inhibiting properties of sulfur compounds become manifest at low optimum



ThiolsSulfidesDisulfidesThiophenes

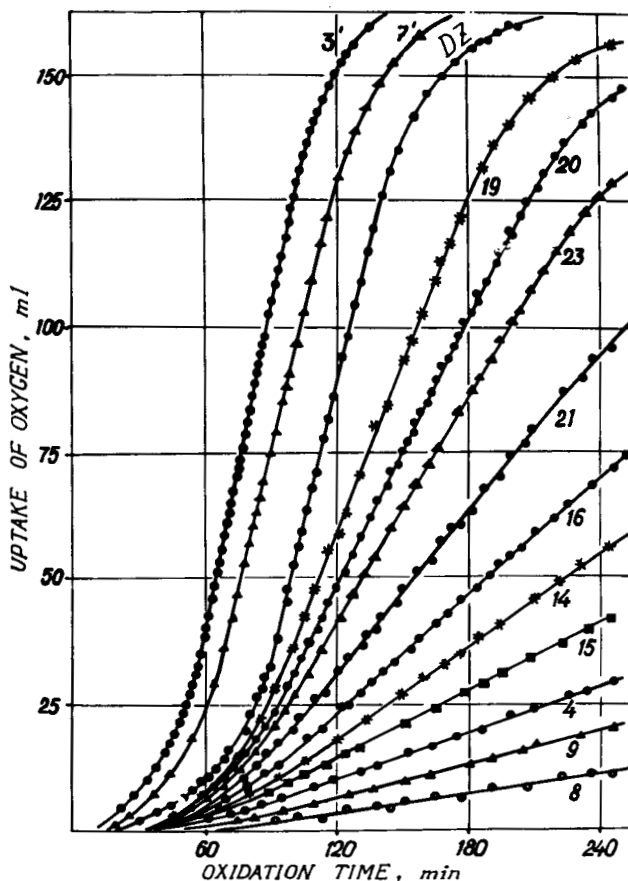


**Figure 3** The effect of sulfur compounds (0.01 wt. %) on the noninitiated oxidation of TS-1 fuel at 150 °C. 7', 8', 9': the sulfur compound concentration constitutes 0.3 wt. % (as recalculated for sulfur).

concentrations (0.01–0.03 wt. %).<sup>1</sup> At higher concentrations the oxidation rate increases, exceeding to a considerable extent the oxidation rate of the pure hydrocarbons (Figs. 2–4). The formation of insoluble oxidation products such as sediments and gums occurs at a greater rate<sup>1</sup>. A series of experiments were conducted to elucidate the mutual effect of the structures of sulfur compounds and of the hydrocarbon medium on the formation of insoluble oxidation products.

Individual sulfur compounds (0.2 wt. % as recalculated for sulfur) were added to individual hydrocarbons. The mixtures obtained were heated in an oxygen atmosphere in air-tight vessels for 6 h at 150 °C at a liquid/vapor phase ratio of 1:10. After the oxidation the amount of sediments and gums insoluble in the oxidation products was determined.

<sup>1</sup>The insoluble oxidation products formed in fuels, especially in those for flying vehicles, are extremely undesirable because of their adverse effect on the vehicle operation reliability<sup>2</sup>.



**Figure 4** The effect of sulfur compounds (0.01 wt. %) on the noninitiated oxidation of DZ fuel at 150°C. 3', 7': the sulfur compound concentration constitutes 0.3 wt. % (as recalculated for sulfur).

Chemical analyses of the sediments formed show that they contain significant quantities of acids (70–90%) which titrate with a distinct potential jump (Table 4).

Oxidation of mixtures containing alkanes, cycloalkanes and linear aliphatic sulfur compounds and thiophanes leads to the formation of sediments whose average molecular weight is 670–810. With decreasing molecular mass of the hydrocarbon medium the molecular mass of the sediment also decreases. Sediments with a similar elemental composition are formed due to the oxidation of hydrocarbon/aliphatic sulfur compound mixtures. On oxidation of these mixtures the least amount of solid phase is formed in the case where the structure of the carbon skeleton of the hydrocarbon medium is similar to that of the sulfur compounds (Table 4). This is exemplified by the oxidation of *n*-hexadecane/1-nonanethiol mixtures. In this case the least amounts of solid particles are formed relative to other mixtures. When the sediment was heated for 2.5 h at 150°C in a specially designed unit particles with a radius of 500–550 Å were formed.<sup>3,4</sup> Thousands of "average" conventional molecules of the sediment are involved in the formation of these particles. The formation of the solid phase occurs solely due to the presence of

**Table 3.** The effect of sulfur compounds on the initiated cumene oxidation at 343 K

Compound number*	(Sulfur compounds) · 10 <sup>2</sup>		K <sub>7</sub> , l/(mole·s)	f	
	as recalculated for sulfur, wt. %	mole/l			wt. %
1	1	0.27	5.0	(0.9 ± 0.2) · 10 <sup>3</sup>	0.09
2	1	0.27	3.9	(1.1 ± 0.3) · 10 <sup>3</sup>	0.11
3	1	0.27	3.4	(1.2 ± 0.4) · 10 <sup>3</sup>	0.13
4	1	0.27	5.0	(1.4 ± 0.3) · 10 <sup>3</sup>	0.18
5	1	0.27	6.8	(1.9 ± 0.5) · 10 <sup>3</sup>	0.30
7	1	0.27	4.3	(2.7 ± 0.3) · 10 <sup>3</sup>	0.33
6	1	0.27	3.9	(2.9 ± 0.3) · 10 <sup>3</sup>	0.35
8	1	0.27	5.7	(8.7 ± 0.7) · 10 <sup>4</sup>	0.52
9	1	0.135	3.3	(43.40 ± 0.6) · 10 <sup>4</sup>	0.98
10	1	0.27	9.0	(0.8 ± 0.3) · 10 <sup>2</sup>	—
11	1	0.27	5.4	(0.9 ± 0.4) · 10 <sup>2</sup>	—
24	1	0.27	5.4	(0.9 ± 0.5) · 10 <sup>2</sup>	—
12	1	0.27	6.7	(1.2 ± 0.3) · 10 <sup>2</sup>	—
13	1	0.27	5.8	(1.4 ± 0.4) · 10 <sup>2</sup>	—
10	10	2.7	89.5	(0.8 ± 0.2) · 10 <sup>3</sup>	0.07
11	10	2.7	53.8	(0.9 ± 0.3) · 10 <sup>3</sup>	0.12
24	10	2.7	53.8	(0.8 ± 0.4) · 10 <sup>3</sup>	0.12
12	10	2.7	67.0	(1.3 ± 0.4) · 10 <sup>3</sup>	0.13
23	10	2.7	60.7	(1.5 ± 0.6) · 10 <sup>3</sup>	0.14
13	10	2.7	58.2	(1.6 ± 0.7) · 10 <sup>3</sup>	0.15
14	1	0.135	4.5	(1.2 ± 0.6) · 10 <sup>2</sup>	—
15	1	0.135	3.4	(1.8 ± 0.5) · 10 <sup>2</sup>	—
16	1	0.135	3.9	(2.1 ± 0.5) · 10 <sup>2</sup>	—
14	10	1.35	45.4	(1.3 ± 0.2) · 10 <sup>3</sup>	0.18
15	10	1.35	34.1	(1.4 ± 0.4) · 10 <sup>3</sup>	0.28
16	10	1.35	38.5	(1.7 ± 0.7) · 10 <sup>3</sup>	0.32
17	3	0.81	17.1	(0.9 ± 0.3) · 10 <sup>2</sup>	—
18	3	0.81	12.6	(1.2 ± 0.4) · 10 <sup>2</sup>	—
19	3	0.81	14.0	(1.8 ± 0.2) · 10 <sup>2</sup>	—
17	20	5.4	113.9	(1.3 ± 0.7) · 10 <sup>3</sup>	0.17
18	20	5.4	83.88	(1.4 ± 0.6) · 10 <sup>3</sup>	0.20
19	20	5.4	93.1	(1.6 ± 0.7) · 10 <sup>3</sup>	0.23
21	12	3.2	76.7	(1.7 ± 0.8) · 10 <sup>3</sup>	0.19
22	12	3.2	85.5	(1.8 ± 0.9) · 10 <sup>3</sup>	0.20

\* See Table 1

oxidized sulfur compounds in the mixture, for no sediment is formed on oxidation of pure alkanes/cycloalkanes. The products formed as a result of oxidation and condensation contain aliphatic chains of considerable length; these compounds should be readily soluble in alkanes and cycloalkanes, especially in *n*-hexadecane. On further condensation, the size of the oxidized molecules increases to hundreds of Ångström and a solid precipitate is formed.

IR spectra taken for the sediments formed by oxidation of mixtures containing a mixture of alkanes and cycloalkanes with aliphatic sulfur compounds display a number of similar bands, which testifies to the occurrence of similar structural groups and bonds.

**Table 4.** Characteristics of the solid phase formed on oxidation of hydrocarbon mixture in the presence of sulfur compounds\*

Sulfur compound number**	Amount of sediment, mg/100 ml	Elemental composition, %				Molecular mass	Total acid number, mg KOH/100 g	Carboxylic acids, wt. %	Sulfonic acids, wt. %
		C	H	S	O				
1	2	3	4	5	6	7	8	9	10
in <i>n</i> -hexadecane									
3	18.7	60.3	9.5	8.2	22.0	579.2	50.1	22.5	77.5
1	187.4	55.2	6.3	11.5	27.0	760.3	48.4	15.7	84.3
14	9.8	61.2	9.8	8.0	23.0	590.4	49.3	17.3	82.7
15	152.7	52.3	6.8	12.0	28.9	786.3	44.3	12.3	87.7
13	9.2	53.9	6.4	11.9	27.8	585.7	46.3	14.3	85.7
10	137.4	62.3	9.2	8.1	20.4	762.8	52.3	17.4	82.6
23	9.4	55.4	6.2	10.9	27.5	593.0	49.1	12.1	87.9
24	9.9	60.9	8.8	8.7	21.4	752.3	48.4	13.1	86.9
11	10.1	61.1	10.0	9.0	19.9	802.0	58.4	20.1	70.9
17	5.8	57.3	6.1	11.8	25.0	595.4	32.4	88.4	11.6
19	87.4	62.2	7.0	10.3	20.5	656.0	46.0	16.1	84.9
in dodecylcyclohexane									
1	18.9	60.9	8.8	8.0	22.3	810.1	52.4	10.1	89.9
14	161.1	62.3	8.5	7.9	21.3	782.1	48.3	17.2	82.8
10	11.2	61.8	7.9	8.1	22.2	792.1	47.8	16.3	83.7
1	190.3	57.3	7.0	10.4	25.3	602.0	47.0	8.4	91.6
13	152.4	58.4	6.4	9.8	25.4	588.0	43.1	16.4	83.6
15	163.8	59.3	6.3	10.2	24.2	608.0	46.4	12.3	87.7
24	10.2	61.4	8.4	8.1	22.1	777.3	42.0	14.3	85.7
19	81.4	60.3	7.2	9.7	22.8	659.0	50.1	14.0	86.0
in alkanes and cycloalkanes isolated from TS-1 fuel									
1	15.6	61.2	8.0	8.2	22.6	754.2	53.4	8.3	91.7
14	12.4	60.3	8.3	8.3	23.1	734.1	50.0	14.3	85.7
10	11.0	60.4	7.8	8.0	23.8	762.4	48.4	16.4	83.6
24	9.9	59.8	7.9	7.9	24.4	732.8	49.0	17.0	83.0
1	194.1	57.4	6.2	9.8	26.6	586.3	47.0	7.0	93.0
13	178.2	58.3	6.2	10.0	25.5	594.0	44.3	16.4	83.6
15	172.6	57.0	6.4	10.9	25.7	597.3	46.2	17.3	82.2
in isopropylbenzene									
1	38.4	57.1	8.3	11.2	23.4	630.4	42.4	24.3	75.7
10	27.5	58.0	8.1	11.5	22.4	627.5	43.4	22.4	77.6
14	32.7	58.7	8.2	10.3	22.8	632.8	40.2	23.8	76.2
3	27.8	60.4	9.6	8.3	21.7	590.3	44.2	17.4	82.6
13	27.4	61.0	9.3	8.2	21.5	578.6	43.8	12.2	87.8
15	20.3	60.8	9.7	8.5	21.0	585.9	42.4	16.3	85.7
19	8.2	62.4	9.8	8.0	17.9	594.2	38.2	32.4	67.6

\* oxidation carried out for 6 h at 150 °C in an oxygen atmosphere at a liquid/vapor phase ratio of 1:10.

\*\* see Table 1.

The IR spectra show intense C–H bands assigned to CH<sub>2</sub> and CH<sub>3</sub> groups of aliphatic compounds (2960, 2920, 2850, 1460, 1380 and 720 cm<sup>-1</sup>).

An absorption of medium intensity shifted to the 1680–1650 cm<sup>-1</sup> region is evidence for C=O ··· HO hydrogen bonds, the C=O group being assigned to esters, acids and ketones (1420 cm<sup>-1</sup>). The sediment spectra show bands in the 3550–3520 and 3450 cm<sup>-1</sup> regions which may be assigned to the stretching vibrations of OH groups linked by an intramolecular hydrogen bond. There are also bands showing the presence of >S≡O

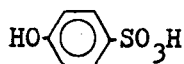
groups assigned to covalent sulfonates of the  $R^1O-SO_2-R^2$  type ( $1420-1330$ ,  $1200-1145\text{ cm}^{-1}$ ). An absorption near  $1130\text{ cm}^{-1}$  must be due to sulfinic esters of the  $R^1-S(=O)-R^2$  type. It should be noted that the sediments contain no sulfones and sulfoxides,

which signifies that the sediment molecules are formed by sulfur compound molecules with broken C-S bonds. The absorption near  $930-1350\text{ cm}^{-1}$  may be due to thioacids and their derivatives.

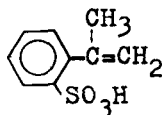
The situation is changed when mixtures of alkanes and cycloalkanes with aromatic sulfur compounds are oxidized. In this case a solid phase is formed the composition and molecular mass of which remain essentially the same irrespective of whether the said mixtures are oxidized in the presence of diphenyl sulfide, diphenyl disulfide, thiophenol or 3-methylbenzothiophene. The sediments formed due to the oxidation of these mixtures have a lower molecular mass ( $560-580$ ) relative to the sediments formed by oxidation carried out in the presence of aliphatic sulfur compounds. Chemical and spectral analyses reveal the similarity of the composition and structure of the sediments formed by oxidation of mixtures containing a mixture of alkanes and cycloalkanes and diphenyl sulfide, diphenyl disulfide, thiophenol and 3-methylbenzothiophene. The composition of the mixture and the structures of the alkanes and cycloalkanes are of minor significance.

The sediment spectra contain absorption bands of high intensity associated with covalent  $R^1OSO_2R^2$  sulfonates ( $1420$  and  $1200\text{ cm}^{-1}$ ), sulfonic acids ( $1150-1200$ ,  $1010-1080$  and  $630\text{ cm}^{-1}$ ), sulfinic acids ( $1090\text{ cm}^{-1}$ ) and sulfinic acid esters ( $1140\text{ cm}^{-1}$ ). Absorption bands due to CH bonds of  $CH_2$  and  $CH_3$  groups ( $2960$ ,  $2920$  and  $2850\text{ cm}^{-1}$ ) are indicative of the fact that alkane and cycloalkane molecules are involved in the formation of the solid phase, some of the chains consisting of four or more  $CH_2$  groups. Since aromatic hydrocarbons contain no such chains, it is a further indication of the role played by the alkanes and cycloalkanes in the formation of the solid phase. However, these bands are of low intensity, which signifies that aliphatic structures play a minor role in the formation of the solid phase. There is unambiguous evidence of the occurrence of benzene rings ( $1620$  and  $3050\text{ cm}^{-1}$ ) and of disubstituted species ( $960-1000$ ,  $735-770\text{ cm}^{-1}$ ). Since the original sulfur compounds contain a monosubstituted benzene ring, the formation of disubstituted species most probably occurs via  $HOC_6H_4SO_3^-$  and  $HOC_6H_4SO_2^-$ . Oxidation of mixtures containing 3-methylbenzothiophene leads to the formation of sediments the spectra of which display a considerable amount of disubstituted benzene rings ( $960-1000$  and  $736-772\text{ cm}^{-1}$ ) and of unsaturated  $R^1R^2C=CH_2$  species ( $885\text{ cm}^{-1}$ ) out-of-plane deformation vibrations being assigned to the C-H bond appearing in the  $885\text{ cm}^{-1}$  region.

Thus, the oxidation of thiophenol, diphenyl sulfide and diphenyl disulfide results in the formation of



species of similar structure, while the oxidation of 3-methylbenzothiophene gives



species which show a strong tendency of oxidative condensation and hence play a significant role in the formation of the solid phase. Aromatic sulfonic acids and phenol-sulfonic acids interact with alcohols and hydroxyacids to give compounds which precipitate on further condensation. The IR spectra taken for the sediments display clearly defined absorption bands of C=O and OH groups (1700–1720 and 3630, 3550–3450, 3400  $\text{cm}^{-1}$ , respectively) assigned to alcohols, ketones, acids and hydroxy acids which were quantitatively determined by chemical methods. The absorption bands of high intensity displayed in the IR spectra around 3400  $\text{cm}^{-1}$  persist even on dilution, which is evidence of the presence of associates linked with intramolecular hydrogen bonds.

Sulfur- and oxygen-containing compounds show a tendency to coagulation when mixtures of these compounds and of aromatic sulfur compounds are oxidized since the oxidation products formed contain aromatic structures capable of association. Due to a striking dissimilarity observed between aromatic sulfur compounds and the hydrocarbon medium with respect to their chemical nature the sediments formed consist of particles of much greater size. The number of particles formed in this case is greater relative to that formed due to the oxidation of mixtures containing aliphatic sulfur compounds, alkanes and cycloalkanes.<sup>2</sup>

Based on the experimental data obtained it can be stated that:

1. Organic sulfur compounds used at optimum concentrations are capable of effectively inhibiting the oxidation of hydrocarbons.

2. Organic sulfur compounds may be arranged in the following order according to their inhibitive properties displayed towards oxidation of hydrocarbons at elevated temperatures: thiophenes < thiophanes (sulfides) < disulfides < thiols. The correlation of the inhibitive properties of sulfur compounds depends to a considerable degree on the structures of their hydrocarbon skeletons.

3. Organic sulfur compounds occurring in hydrocarbon fuels tend to enhance the formation of insoluble oxidation products in these fuels. The amount of oxidation products formed depends on the structures of the sulfur compounds and of the hydrocarbon medium.

4. When the structure of organic sulfur compounds is close to that of the hydrocarbon medium (ArS-Ar, AlkS-Alk) the least amounts of insoluble oxidation products are formed; however, when the structures of the sulfur compounds differ significantly from that of the hydrocarbon medium (ArS-Alk, AlkS-Ar) large amounts of these products are formed.

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