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SYNTHESIS OF NEW SULFUR-, PHOSPHORUS-CONTAINING COMPOUNDS AS ADDITIVES TO TRANSMISSION OILS AND DIESEL FUELS

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Abstract. The literature contains extensive material on the synthesis of sulfur- and sulfur-phosphorus-containing compounds used as additives for various purposes to fuels and lubricants. However, interest in these additives has not decreased to this day, which is associated with the increasing modernization of equipment used in all industries, which requires the creation of new lubricating oils and therefore a new generation of additives. Thus, the need to synthesize new compounds of practical value is a pressing problem in petrochemistry. The aim of this work is to synthesize new esters, xanthogenates, dithiophosphates and the well-known (bisphenolsulfo)disulfide obtained from arylsulfonylchlorides, which are readily available compounds characterized by high reactivity and salts of alkylxanthogenates, dithiophosphoric acids and alkali metal sulfides, which are also readily available synthons, followed by their investigation as extreme pressure and anti-wear additives to transmission lubricants and antioxidants to diesel fuel. The originality of the work lies in the synthesis of p-toluenesulfonylbutylxanthogenate, p-phenolsulfoisopropylxanthogenate, 1-3(bisizopropylxanthogenatesulfo)phenol and p-toluenesulfoisopropyl dithiophosphate. Previously, the authors of the article synthesized and studied a large number of esters of xanthogen dithiophosphoric acids and disulfides, but those containing arylsulfo groups were synthesized for the first time. The novelty of the compounds was confirmed by Yusif Abdullayev, a scientist from Azerbaijan at Allan University in South Carolina, USA, based on the results of a check conducted on the global search engine "SciFinder". Four patents were received for the work done and the research results were presented at international conferences. Based on these compounds, fairly effective anti-wear additives for transmission oils have been developed. It has been found that *p*-toluene sulfoisopropyl dithiophosphate has additional anti-wear properties, which is an important factor for transmission oils, while *p*-phenolsulfoisopropyl xanthogenate and 1,3-(bis-isopropylxanthogenate sulfo)phenol have dual-action additive properties, i.e., they effectively inhibit the oxidation of the model hydrocarbon cumene, which can serve as a basis for the creation of highly efficient diesel fuels. Due to their limited solubility in mineral oils, *p*-phenolsulfoisopropylxanthogenate and bis(phenylsulfodisulfide) were studied in synthetic and semi-synthetic oils, but they also have high anti-seize properties. The tribological properties were studied on a four-ball friction machine (FFM-1).

Keywords: *Additives, tribological properties, antioxidants, diesel fuels.*

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1. Introduction

Studying the literature on the synthesis and application of sulfur- and sulfur-phosphorus-containing compounds, it can be stated that these compounds are successfully used in various fields of national economy (Moskvichev *et al*., 2005; Yakimova, 2003; Khaidarov *et al*., 2006; Mustafaev *et al*., 2022).

One of the important areas of their application is their use as additives for various purposes to lubricating oils (Zakharov *et al*., 2016; Aleksanyan *et al*., 2017; Farzaliev *et al*., 2015, 2023).

As it is known, there are different types of lubricating oils according to their purpose and field of application, one of them is gear oils. Due to the development of machine building, as well as other industries, the need for these oils is growing from year to year, so the creation of new additives is a very relevant issue of the present time.

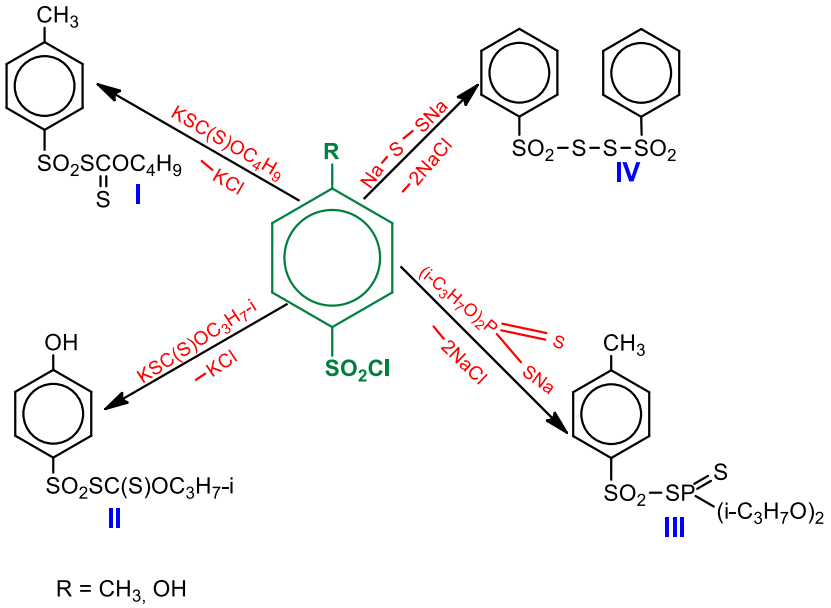
One of the main requirements for transmission oils is their high tribological properties, which are imparted to them mainly due to sulfur- and sulfur-phosphorus-containing additives. The most effective among them are derivatives of xanthogenic, dithiophosphoric acids and sulfides. The authors of the article have extensive experience in the synthesis of such compounds (Mustafayev *et al*., 2015; Mustafaev *et al*., 2017, 2019; Musaeva *et al*., 2015).

This work is devoted to the synthesis of new compounds that could be included in the additive package as extreme pressure and anti-wear components to improve the properties of transmission oils. This goal was achieved by synthesizing aryl sulfoxanthogenates, diisopropyl phytophosphates and disulfides, which have not been previously described in the literature. The interest in compounds containing arylsulfoxyl fragments can be explained, on the one hand, by the fact that when synthesizing additives, it is necessary to take into account not only their high tribological properties, but also the availability of the starting reagents used in their synthesis. As can be seen from the diagram, the compounds are synthesized on the basis of arylsulfochlorides and xanthogenates, dithiophosphates and alkali metal disulfides, many of which are commercial products. It should be noted that arylsulfonyl chlorides are widely used starting compounds for the production of products used as insecticides, pharmaceuticals, dyes, etc. (https://xumuk.ru/encyklopedia/2/4514.html; Farzaliev *et al*., 2002), while there is virtually no information in the literature on their use as additives to lubricating oils.

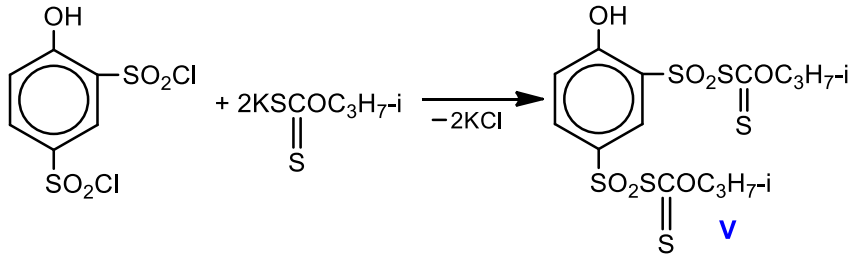
By comparing the structure and fragment composition of known antioxidants (Farzaliev, 2007; Kuramshin & Imashev, 2012) with synthesized compounds, some of them were investigated as inhibitors of diesel fuel oxidation.

As is well known, the presence of unsaturated hydrocarbons in fuels and lubricants or the use of low-quality raw materials for their production leads to the oxidation of fuel components, which affects both its commercial appearance and its operational properties. Therefore, antioxidants containing radical chain oxidation inhibitors are added to fuels and lubricants used in modern engines. Compounds of various classes are used as antioxidants: phenols, sulfur, nitrogen and phosphorus compounds (https://www.chimtec.ru/info/articles/okislenie-topliv).

The synthesis of a number of new sulfur- and sulfur-phosphorus-containing compounds is presented in the following schemes:



Scheme 1.



Scheme 2.

As follows from the relevant periodical literature, there are currently major problems with conducting experiments and reproducing research in science (Vorontsov *et al*., 2021). It should be noted that the authors of this work have practically no problems in this area, which is quite understandable: the starting reagents are widely available.

p-Arylsulfonyl chlorides readily undergo nucleophilic substitution reactions, in which halogens in arylsulfonyl chlorides are replaced by alkylxanthogenate, diisopropyl dithiophosphoric acid and disulfides. The experimental setup is described in detail and all physicochemical and spectral analyses confirming the composition and structures of the compounds are presented.

2. Materials and Methods

2.1. Determination of the individuality of the compounds obtained

The identity of the compounds obtained was confirmed by determining their elemental composition; the elements C, H, S and P were determined using a TruSpec-Micro analyzer (LECO), refractive index (n_D^{20}), specific gravity (d_4^{20}) with subsequent MR_D calculations and comparison, as well as IR, NMR spectroscopy and chromatography-mass spectrometry and MRD calc. and their comparison, as well as IR and NMR spectroscopy and chromatography-mass spectrometry.

2.2. Determination of chemical composition

IR spectra were recorded on a SPECORD-75 IR spectrophotometer (Carl Zeiss, GDR) using KBr, NaCl and Lif prisms in the range of 4000÷400 cm^{-1}.

The ^{1}H and $^{C}13$ NMR spectra were recorded at 20°C on a BRUKER-Fourier-NMR spectrometer (300 MHz) using deuterated benzene as a solvent and tetramethylsilane (TMS) as an internal standard.

2.3. Method for studying the component composition of the compounds under investigation

The QX-KS method (gas chromatography with mass spectrometry) was used to study the component composition of the compounds under investigation. For this purpose, an Agilent Technologies 6890N Network CG System was used, with a 5975 inert Mass Selective Detector, Split/Splitless, injection -Split, Inlet pressure 60.608 kpa, Split-100, Low Mass-40, High Mass-400, Threshold 150.

The analysis conditions are as follows: on capillary columns with dimensions (30 m × 0.25 mm) filled with a stationary liquid phase, HP-1 silicone elastomer thermostated at a programmed temperature of 50-3000C, purged with nitrogen carrier gas at a rate of 1.0-2.0 ml/min.

2.4. Determination of tribological properties

Tribological properties were determined according to GOST 9490-75. The calculated indicators were the load wear index (LW_I) (*load wear index* - an indicator indicating the effectiveness of extreme pressure properties in the interval between the welding load and the seizing load; the higher this indicator the better), critical load (C_L) (*seizing load* - the mode in which the oil film and sliding of rubbing surfaces becomes difficult; in this case, the hydrodynamic friction mode is replaced by a semi-dry friction mode), welding load (W_L) (*welding load* – is the force at which the rubbing surfaces are not able to slide relative to each other; moreover, high specific loads cause critical increase in temperature in the direct contact zone, which, in turn, entails welding of the contacting surfaces), wear spot diameter (W_d) (characteristic of anti-wear properties).

Given that when studying the tribological properties of joints on a four-ball friction machine (FFM-1), there are possible sources of error: errors in measuring instruments; the influence of conditions; errors in the data processing algorithm, etc., the samples were manufactured and studied repeatedly to ensure the accuracy of the experimental results. Then, the average values were calculated for each indicator, i.e., for the seizure load (C_L), welding load (W_L) and scuffing index (LW_I). The results of the data obtained were then presented in Tables 1 and 2.

2.5. Antioxidant properties

The antioxidant properties were studied using a manometric apparatus with automatic pressure control. Azodibutyronitrile was used as an initiator. The catalytic action indicates the chain nature of oxidation. The chain reaction rate can be increased by adding small amounts of certain inhibitors to the reaction mixture. The action of inhibitors is that inhibitor molecules react with free radicals leading the chain (Farzaliyev *et al*., 2023).

To verify the reliability of the data when determining the antioxidant properties by the cumene oxidation method, standard antioxidants (ionol) were used. The experiments were repeated using different concentrations of compounds. The reactions were carried out at 60^0C, using α,α′-azodibutyronitrile (ABIN) was used as an initiator. The initiator was introduced at a concentration of $2 \cdot 10^{-2}$ mol/l and the inhibitor concentration was varied in the range from $1 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ mol/l.

The setup used to perform the presented work on the synthesis of new compounds consisted of a glass three-necked flask equipped with a thermometer, a dropping funnel and a mechanical stirrer heated by an electric flask heater.

3. Experimental

3.1. ***Syntheses of p-toluenesulfobutylxanthogenate (I)*** (Kazimzadeh *et al*., 2022)

To 18.8 g (0.1 mol) of potassium butylxanthogenate stirred in aqueous medium at 25ºC was added 19.1 g (0.1 mol) of *p*-toluenesulfochloride in portions, the temperature was raised to 40ºC, stirring was continued for 3h at 60ºC. The product was extracted with benzene, the extract was washed with water, the benzene was distilled off and dried under vacuum. The yield was 23 g (85 %). Let's proceed to the physicochemical characteristics and elemental analysis of the synthesized product:

n_D^{20} – 1.5810; d_4^{20} – 1.2571; MR_D found. – 80.6; MR_D calc. – 81.1

Group $C_{12}H_{16}O_3S_3$: Found, %: C – 52.86; H – 6.14; S – 23.41

Calculated, %: C – 52.91; H – 5.92; S – 23.55

In the IR spectrum of *p*-toluenesulfobutylxanthogenate (Figure 1), the absorption bands of out-of-plane deformation vibrations in the aromatic core ν_{C-H} are 653 cm^{-1}, 742 cm^{-1}, 819 cm^{-1} and 910 cm^{-1}; the absorption bands $\nu_{S=O}$ 1026.70 cm^{-1} and the absorption bands of bond vibrations $\nu_{C=S}$ at 1136 cm^{-1}, 1259,78 cm^{-1}.

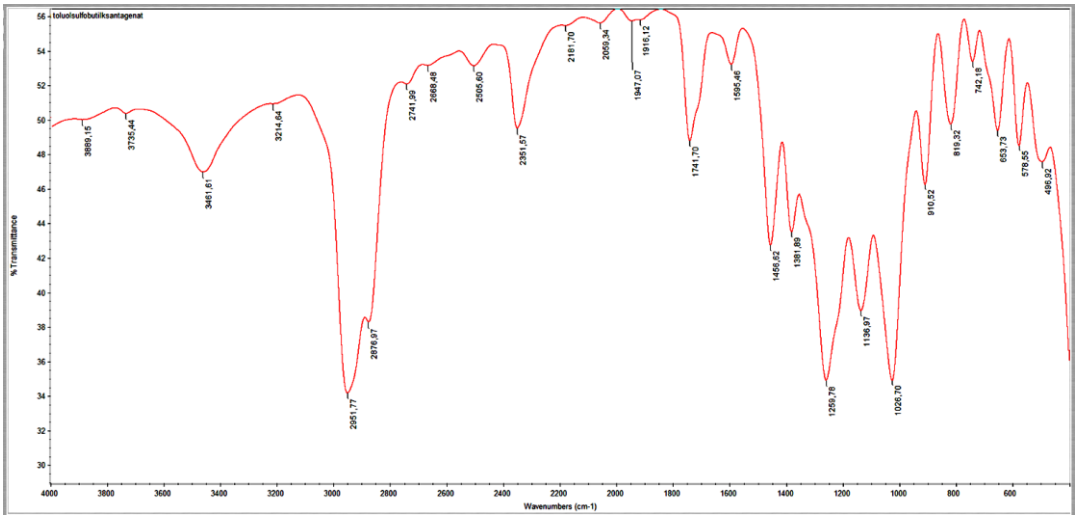


Figure 1. IR spectrum of *p*-toluenesulfobutylxanthogenate

It should be noted that the work of authors engaged in IR spectral studies of xanthogenic acid esters confirms the reliability of obtaining arylsulfoxanthogenates. Little et al. (1961) believe that xanthogenates correspond to a series of bands in the ranges 1250-1200; 1140-1110, as well as 1070-1020 cm^{-1} (C = S). However, the introduction of

additional functional groups can lead to a change in the intensity and frequency of absorption of the valence vibrations of the C = S group. In addition, xanthogenic acid esters are also characterized by absorption bands of the C – S group. According to Bellami (1971), it is recommended to use weak bands in the 700-600 cm^{-1} range to identify this group. The presence of S = O groups in the synthesized compounds is also confirmed by data presented in the literature (Grinenko *et al*., 2015).

The NMR spectrum of p-toluenesulfonylbutyl xanthogenate (**I**) was also recorded.

^{1}H ЯМР (BRUKER-Fourier 300 MHs, C_6D_6, δ, m.h.): 0.98 (d., 6H, CH_3, J=6.3 Hz), 1.83 (s., 3H, Ar-CH_3), 5.44 (m., 1H, CH), 6.62 (d., 2H, Ar. J=8.4 Hz), 7.58 (d., 2H, Ar., J=8.4 Hz) (Figure 2).

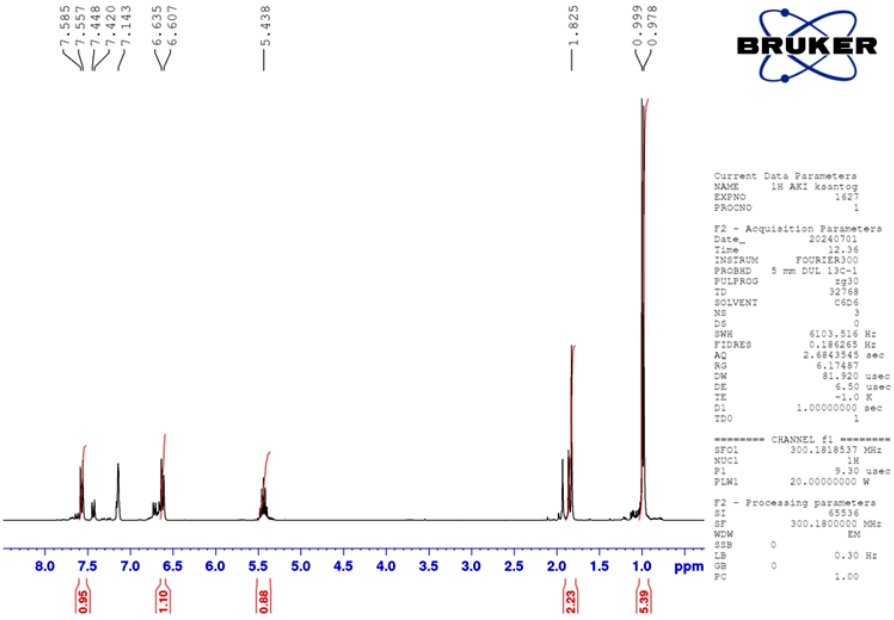


Figure 2. ^{1}H NMR spectrum of *p*-toluenesulfobutylxanthate **(I)**

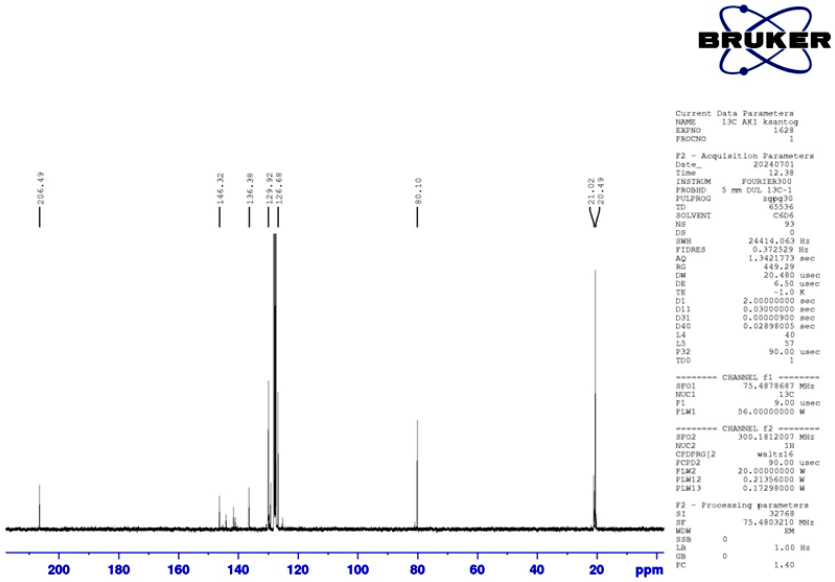


Figure 3. ^{13}C NMR spectrum of *p*-toluenesulfobutylxanthate **(I)**

^{13}C ЯМР (BRUKER-Fourier 75 MHs, C_6D_6, δ, m.h.): 20.49 (CH-CH_3), 21.02 (Ar-CH_3), 80.10 (CH), 126.68, 129.92, 136.38, 146.32 (Ar), 206.49 (C=S) (Figure 3).

3.2. Syntheses of p-phenolsulfoisopropylxanthogenate (II) (Farzaliyev *et al.*, 2025)

To 17.4 g (0.1 mol) of potassium isopropylxanthogenate stirred in aqueous medium was added 19.1 g (0.1 mol) of *p*-phenolsulfochloride. The reaction mixture was stirred for 4 hours at 55-60°C. The obtained product was extracted with benzene, the extract was washed with water, the benzene was distilled off, the residue was dried under vacuum. *p*-phenolsulfoisopropylxanthogenate was a crystalline product. Tmp. – 53-54°C.

Elemental analysis of the synthesized product:

Group $C_{10}H_{12}O_4S_3$: Found, %: C – 41.15; H – 4.03; S – 32.78

Calculated, %: C – 41.08; H – 4.14; S – 32.90

In the IR spectrum of *p*-phenolsulfoisopropylxanthogenate (Figure 2), the absorption bands of the valence vibrations of the bond ν_{C-H} in the aromatic nucleus are 3179 cm^{-1}; the absorption bands of the valence vibrations of the bond C–O belonging to the Ar–OH group are 1268 cm^{-1}; the absorption bands of the valence vibrations of the bond $\nu_{C=S}$ at 666.19 cm^{-1} and the pologues of the valence vibrations of the bond $\nu_{S=O}$ at 1184 cm^{-1}.

In the IR spectrum of *p*-phenolsulfoisopropylxanthate (Figure 4), the absorption bands of the stretching vibrations of the ν_{C-H} bond in the aromatic nucleus are 3179 cm^{-1}, Ar–OH 3445.78 cm^{-1}; the absorption bands of the stretching vibrations of the C–O bond, belonging to the group 1373.38 cm^{-1}; the absorption bands of the stretching vibrations of the $\nu_{C=S}$ bond at 638.71 cm^{-1}.

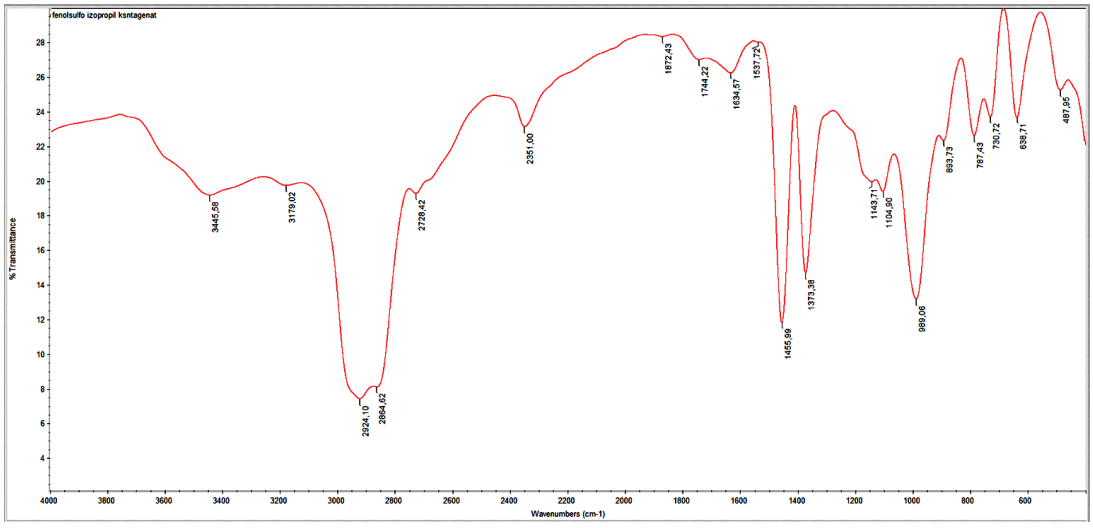


Figure 4. IR spectrum of *p*-phenolsulfoisopropylxanthogenate **(II)**

The identification of *p*-phenolsulfoisopropylxanthogenate (**II**) was also confirmed by chromatography-mass spectrometry.

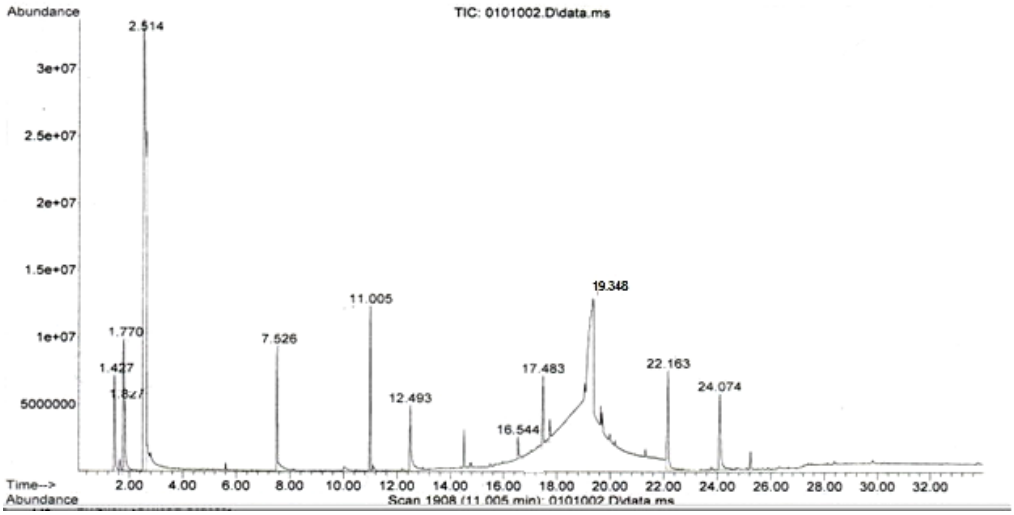


Figure 5. Chromatogram of the composition of the components of the synthesized *p*-phenolsulfoisopropylxanthate **(II)**

Table 1. Composition of the components of *p*-phenolsulfoisopropylxanthate

No	Components	RT	Mass, %
1	$C_2H_{14}OS_2$	1.427	8.77
2	CS_2	1.77	13.11
3	$C_3H_8O_3$	1.827	5.60
4	C_6H_6	2.514	50
5	$C_3H_4S_3$	7.52	11.54
6	$C_7H_{14}OS_2$	11.005	9.91
7	C_6H_6OS	12.493	9.07
8	$C_{12}H_{10}O_4S$	24.074	10.09

In Figure 5, the composition of the components of the g-phenolsulfoisopropylxanthate compound was investigated based on GC=-MS analysis. The main purpose of the analysis is to analyze the components in the compound. As a result of the analysis, a total of 8 main components were identified, their release times and mass fractions were determined. The release of the main solution $C_{10}H_{12}O_4S_3$ in 24.074 minutes confirms that it has a high molecular weight.

The detected CS_2 (13.11%) C_3H_4S (11.54%) and other substances were evaluated as intermediate products formed during the synthesis.

The obtained results confirm the presence of the main product ($C_{10}H_{12}O_4S_3$) in the synthesized sample.

3.3. Syntheses of p-toluenesulfodiisopropyldithiophosphate (III)

(Novotorzhina *et al*., 2024a)

To the stirred 21.4 g (0.1 mol) of diisopropyldithiophosphate was added 10 g of 40 % aqueous NaOH solution, the mixture was stirred for 3 hours at 50°C and then 19.1 g (0.1 mol) of *p*-toluenesulfochloride was added to the flask and stirred for 5 hours at 70°C. A crystalline product (*p*-toluenesulfodiisopropyldithiophosphate) was obtained. The yield was 25.3 g (70 %). Tmp. is 70-72°C.

Elemental analysis of the synthesized product:

Group: $C_{13}H_{21}O_4S_3P$: Found, %: C – 46.21; H – 6.18; S – 28.00; P–8.76

Calculated, %: C – 46.43; H – 6.25; S – 28.10; P–9.00

In the IR spectrum of *p*-toluenesulfodiisopropyl dithiophosphate (Figure 6), the bond absorption bands of the P–O–C_3H_7-i fragment are 1079.77 to 973.93 cm^{-1}; the absorption bands of the valence vibrations of the $\nu_{P=S}$ bond are 806.54 to 638.85 cm^{-1} and the absorption bands of the valence vibrations of the SO_2 group at 1593-1538.87 cm^{-1}.

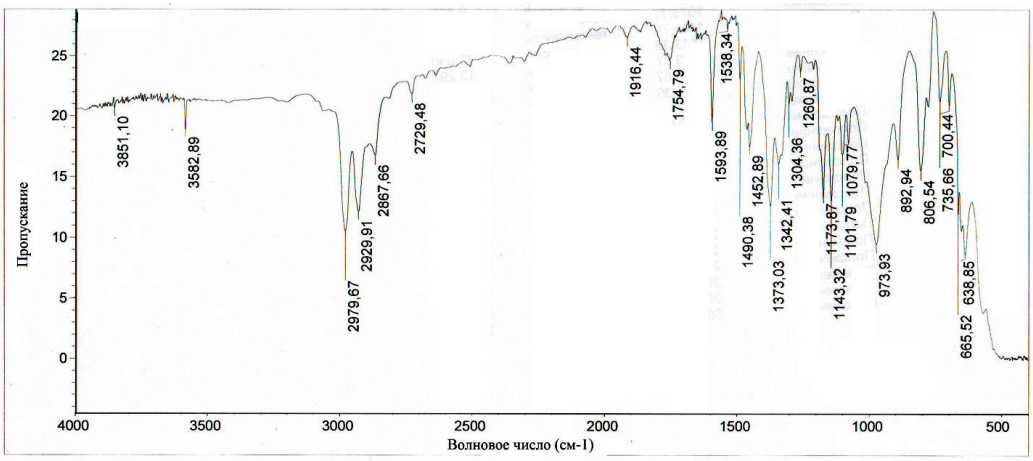


Figure 6. IR spectrum of *p*-toluenesulfodiisopropyldithiophosphate

The absorption bands P=S and P – O – CH_3 are consistent with the data from Bellamy (1971) and Bolshakov et al. (1967).

NMR spectrum of p-toluenesulfonylisopropyl dithiophosphate (**III**)

^{1}H ЯМР (BRUKER-Fourier 300 MHs, C_6D_6, δ, m.h.): 1.14-1.19 (m., 12H, CH-CH_3), 1.73 (s., 3H, Ar-CH_3), 4.84 (m., 1H, CH), 6.51 (d., 2H, Ar. J=8.4 Hz), 7.56 (d., 2H, Ar., J=8.4 Hz) (Figure 7).

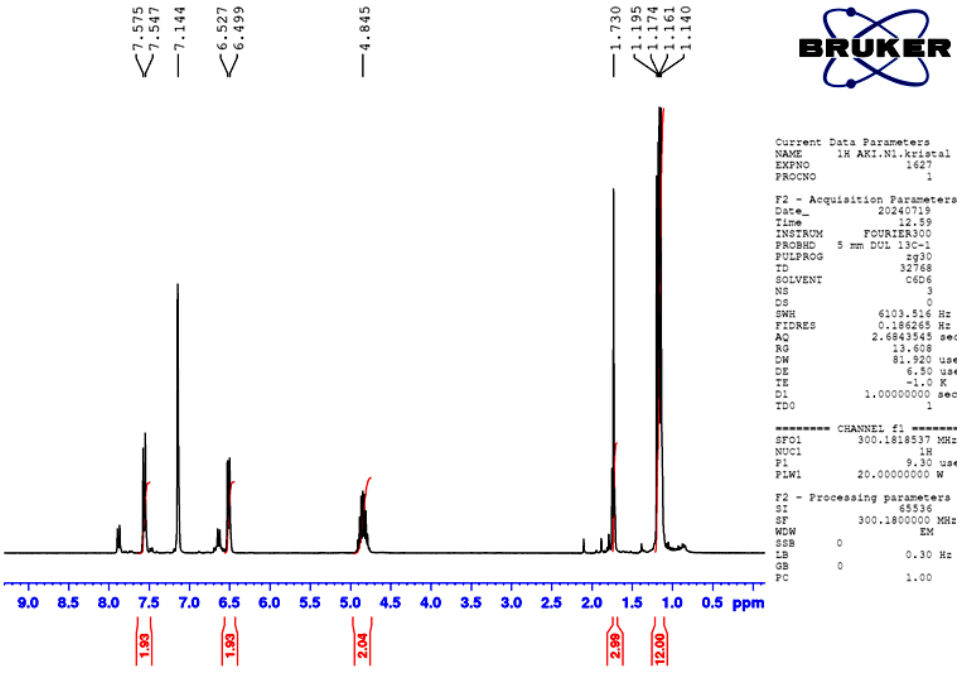


Figure 7. ^{1}H NMR spectrum of *p*-toluenesulfodizopropyldithiophosphate **(III)**

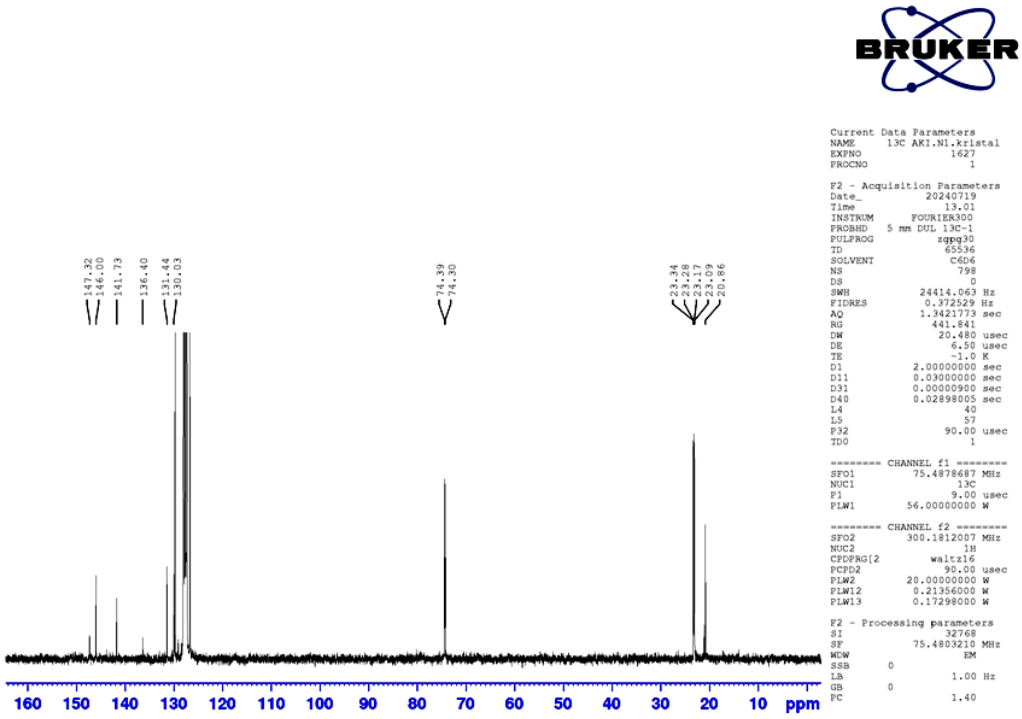


Figure 8. ^{13}C NMR spectrum of *p*-toluenesulfodizopropyl dithiophosphate **(III)**

^{13}C ЯМР (BRUKER-Fourier 75 MHs, C_6D_6, δ, m.h.): 20.86 (Ar-CH_3), 23.09, 23.17, 23.28, 23.34 (CH_3), 74.30, 74.39 (CH), 130.03, 131.44, 141.73, 146.00 (Ar) (Figure 8).

3.4. Syntheses of (bisphenylsulfo)disulfide (IV) (Novotorzhina *et al*., 2024b)

To 7.9 g (0.035 mol) of sodium sulfide stirred in water was added 1.1 g (0.035 mol) of sulfur and stirred for 1 hours at 60°C. Then 11.6 g (0.066 mol) of benzene sulfochloride was added to the flask and stirring was continued for 4 hours. The resulting product was extracted with benzene, washed with water distilled off the benzene and dried under vacuum. The yield amounted to 8.6 g (75 %).

Physicochemical characterization and elemental analysis of the product:

n_D^{20} – 1.5350; d_4^{20} – 1.3724; MR_D found. – 78.48; MR_D calc. – 78.96

Group $C_{12}H_{10}O_4S_4$: Found, %: C – 41.38; H – 2.85; S – 36.82

Calculated, %: C – 41.52; H – 2.91; S – 36.94

In the IR spectrum of (bisphenylsulfo)disulfide (Figure 9), the absorption bands of the valence vibrations of ν_{C-H} in the aromatic core are 3095-3066 cm^{-1}; the absorption bands of the valence vibrations of the bond $\nu_{S=O}$ are 1186 cm^{-1}, 1144 cm^{-1}; the absorption bands of ν_{C-S} are 761 cm^{-1}.

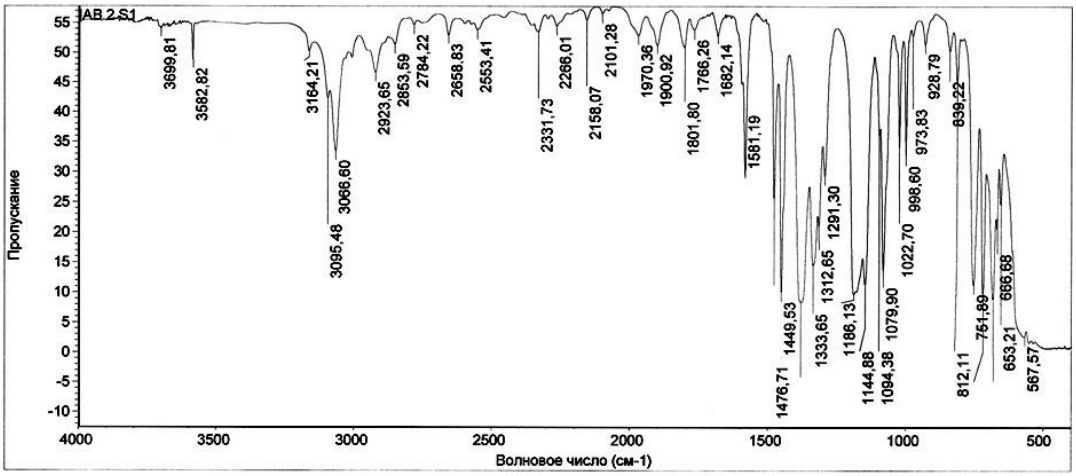


Figure 9. IR spectrum of (bisphenylsulfo)disulfide

NMR spectrum of (bisphenolsulfo)disulfide **(IV)**

^{1}H ЯМР (BRUKER-Fourier 300 MHs, C_6D_6, δ, m.h.): 6.71-6.97 (m., 6H), 7.45 (d., 1H, J=7.2 Hz), 7.54 (d., 1H, J=7.2 Hz), 7.69-7.75 (m., 2H) (Figure 10).

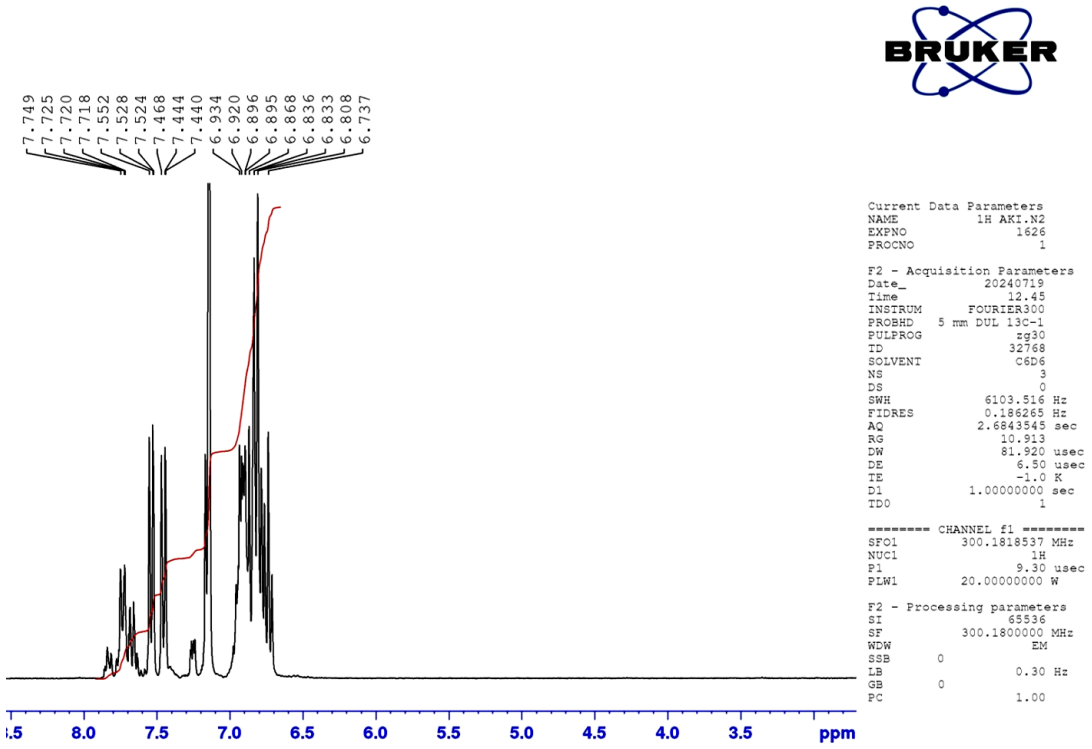


Figure 10. ^{1}H NMR spectrum of (bisphenylsulfo) disulfide **(IV)**

^{13}C ЯМР (BRUKER-Fourier 75 MHs, C_6D_6, δ, m.h.): 128.48, 129.22, 130.87, 134.34, 136.42, 141.48 (Figure 11).

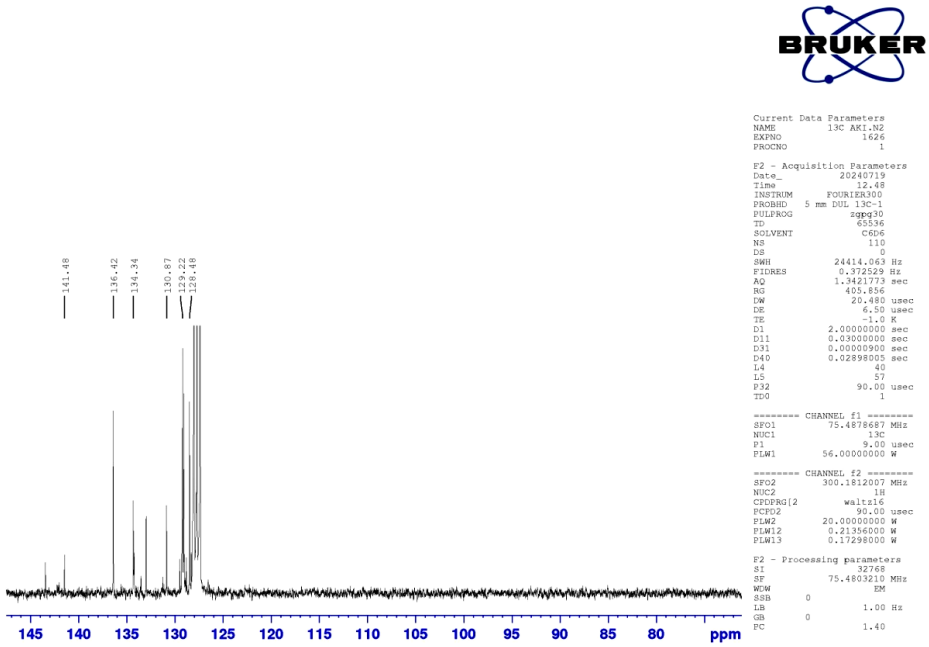


Figure 11. ^{13}C NMR spectrum of (bisphenylsulfo)disulfide **(IV)**

3.5. Syntheses of 1,3-(bisisopropylxanthogenatosulfo)phenol (V)

(Sujayev *et al*., 2025)

To 34.8 g (0.2 mol) of potassium isopropylxanthogenate stirred in 50 ml of water, 19.1 g (0.1 mol) of *p*-phenolsulfochloride was added in portions and stirred for 4 hours at 55-60ºC. The resulting product was extracted with benzene, washed with water and dried under vacuum. The yield amounted to 37.8 g (72 %).

Elemental analysis of the synthesized product:

Group $C_{14}H_{18}O_7S_6$: Found, %: C – 34.17; H – 3.56; S – 39.03

Calculated, %: C – 34.29; H – 3.67; S – 39.20

The –SC(S)– band is the main fragment of the compound. The valence vibration absorption bands of C=S are observed in the region of 938.97–1089 cm^{-1}; the valence vibration absorption band of C–S at 666.35 cm^{-1} and the valence vibration absorption band of the bonding group S=O at 1185.85 cm^{-1} (Figure 12).

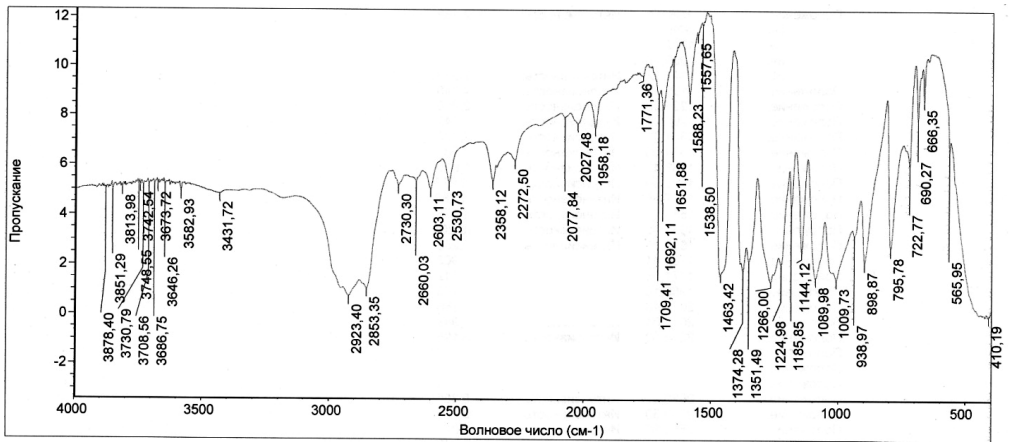


Figure 12. IR spectrum of 1,3-(bisisopropylxanthogenatosulfo)phenol **(V)**

Identification of 1,3-(bisisopropylxanthogenatosulfo)phenol (V) was confirmed by chromatograph mass spectrometry

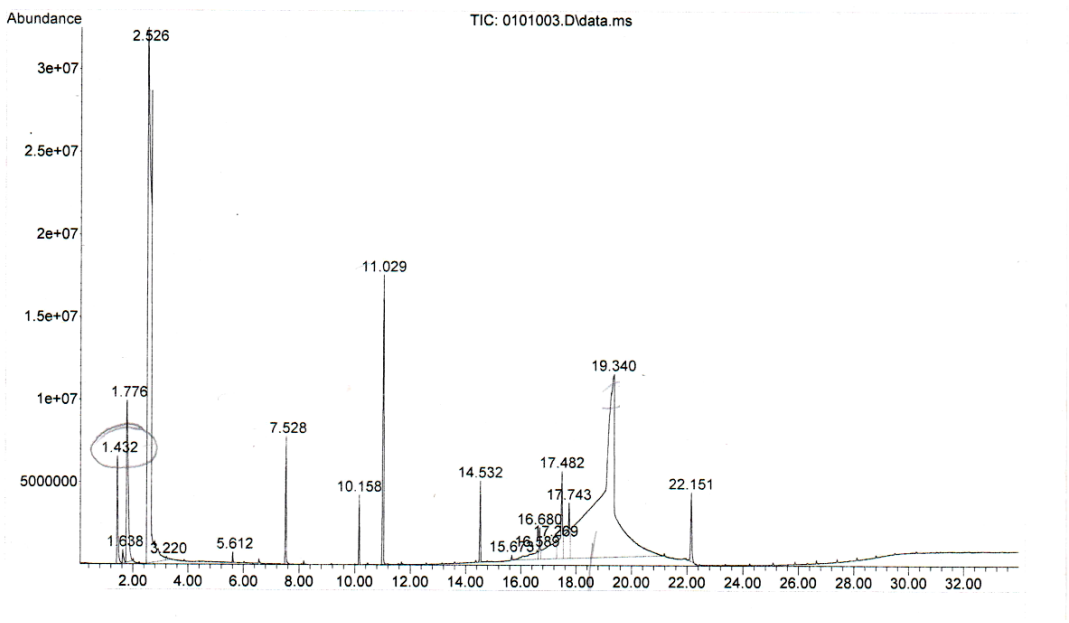


Figure 13. Chromatogram of the composition of the components of the synthesized 1,3-(bisisopropylxanthogenatosulfo)phenol (**V**)

Table 2. Composition of components 1,3-(bisisopropylxanthogenatosulfo)phenole (V)

No	Components	RT	mass, %
1	COS	1.432	1, 66
2	CS_2	1.638	0,22
3	C_6H_6	1,776	4,41
4	C_6H_6	2,526	27,47
5	C_6H_6	3,220	0,10
6	C_8H_{10}	5,612	0,10
7	$C_3H_4S_3$	7,528	1,48
8	$C_7H_{14}OS_2$	11,029	4,39
9	$C_6H_{14}S_2$	14,532	1,10
10	$C_8H_{18}S$	15,673	0,10
11	$C_3H_4S_3$	16,589	1,16
12	$C_{10}H_{14}O_3S$	16,680	0,54
13	$C_3H_4S_3$	17,269	2,70
14	$C_3H_4S_3$	17,482	2,62
15	$C_3H_4S_3$	17,743	2,68
16	$C_6H_{14}S_2$	19,340	47,61
17	S_8	22,151	1,19

The chromatogram presented in Figure 13 shows the Retention Time (RT) indicators of the decomposition products of the substance. The substance $C_6H_{14}S_2$ is the main component with 47.61%. This indicates a high purity of the synthesized product. Various sulfur-containing components with small mass percentages are side and intermediate products.

The analysis of S_8-sulfur as a molecular form indicates the presence of elemental sulfur in the reaction mixture.

4. Results and Their Discussion

4.1. Results of research into extreme pressure properties

When studying the tribological properties of the synthesized compounds, the authors used MC-20 aviation oil, which can also be used to make transmission oils and due to the limited solubility of some additives in mineral oils, they used synthetic PEE oil (penitaterite ether with monobasic carboxylic acids) and semi-synthetic oil, which is a mixture of MC-20 and PEE oils taken in a 1:1 ratio. Thus, p-phenolsulfoisopropyl xanthogenate is insoluble in mineral oils, but soluble in synthetic (PEE – pentaerythritol ester) and semi-synthetic (MS-20:PEE) (1:1) oils.

Table 3 presents the results of testing the extreme pressure properties of p-phenolsulfoisopropylxanthogenate (II) and (bisphenolsulfo)disulfide (IV).

Table 3. Results of investigation of extreme pressure properties of compounds in synthetic and semi-synthetic oils

Compounds	Concentration of samples in oil, %		Extreme pressure properties GOST 9490-75		
	synthetic oil	semi-synthetic oil	Load wear index, LW_I, N	Critical load, C_l, N	Welding load, W_l, N
Synthetic oil (PEE)	–	–	294	508	980
Semi-synthetic oil – MS-20:PEE (1:1)	–	–	283	686	980
II	–	1.5	539	789	2450
	1.5	–	454	784	2548
IV	–	1,5	610	980	3479
—″—	–	3	740	1235	3920

Base oils play a major role in the development of high quality lubricants. For the production of lubricants mainly mineral (petroleum) and synthetic oils are used, to which additives or their compositions are added. Sometimes compounding is done to improve the properties of mineral oils as well as the solubility of additives.

Base oils differently perform the role of additive carrier, the same additives in one of the lubricating oils can give it high extreme pressure properties, in other oils can even dissolve limitedly, in this connection for fulfillment of the set task a careful selection of base oils is necessary. Based on extensive experience in the field of synthesis of extreme pressure additives for lubricating oils, the dependence of solubility of hydroxyl-containing compounds on the presence of additional functional groups in the molecule has been established.

As can be seen from Table 3, all synthesized compounds have sufficiently high anti-seize properties. However, as can be seen from the test results presented, all quantitative indicators corresponding to LW_I, C_l and W_l of aryl sulfoxanogenate are inferior to those of aryl disulfide. To confirm this quantitative information, we should refer to qualitative information, i.e., in this case, information about the mechanism of action of additives.

Thanks to the provided mechanisms of action of xanthic acid esters and disulfides, we can explain the high extreme pressure effectiveness of these compounds.

Currently, there is no consensus on the mechanism of action of xanthogen acid esters as extreme pressure additives to lubricating oils.

According to one version, the high extreme pressure effectiveness of xanthogenates is explained by the presence in the molecule of the –SC(S)– fragment containing both thione and thiol sulfur, which, under increased loads and temperatures, are adsorbed on the metal surface, forming chemically modified protective layers consisting mainly of metal sulfides, which reduce friction and as a result, wear of rubbing surfaces (Novotorzhina *et al*., 2023).

Another version is based on the decomposition, under the influence of high temperature and pressure, of molecules adsorbed on the metal surface into smaller fragments with significant reactivity. In the case of xanthogenates, these are sulfur, mercaptans, xanthogenic acids, etc., which interact with the metal surface at elevated temperatures to form a durable protective layer (Zakharchenko, 2013).

The extreme pressure properties of p-phenoliso-propylxanthogenate can be explained not only by the presence of the –SC(S)– fragment in the molecule, but also by the easily breakable S–S (http://chemteq.ru/articles/prisadki.html), followed by the formation of an additional protective layer consisting of iron sulfides on the metal surface. The introduction of (bisphenolsulfo)disulfide into the oil significantly increases its critical seizing load (S_l) and accordingly, the calculated index (C_i), which determines the extreme pressure efficiency of the additive, which is quite explainable by the presence of the –S–S–S–S– bond in the molecule, which under harsh operating conditions of rubbing parts in an oil environment (temperature, pressure), as the elongation of the chain of sulfur atoms increases the probability of its rupture due to a decrease in bond energy (Tobolsky, 2007).

As a result, the molecule rapidly decomposes and small decomposition molecules interact with the metal surface, which explains the higher anti-seize effectiveness of (bisphenolsulfo)disulfide.

Table 4. Tribological characteristics of synthesized compounds in MS-20 oil

Compounds	Concentration of samples in oil, %	Tribological characteristic to GOST 9490-75			
		Load wear index, LW_I, N	Critical load, C_l, N	Welding load, W_l, N	Wear spot diameter, W_d, mm
MS-20 oil	–	330	794	1568	0.85
I	5	630	882	3920	0,80
III	1.5	560	1235	3097	0.48
V	5	670	980	3980	0.90

Table 4 presents the synthesized compounds soluble in MS-20 mineral oil. *p*-Toluenesulfodiisopropyl dithiophosphate, due to limited solubility, was studied at 1.5% concentration, but despite the relatively small concentration, this compound shows high extreme pressure efficiency.

Based on the research of a number of specialists in the field of extreme pressure additives to lubricating oils, a conclusion was made about the advisability of using low concentration extreme pressure additives, since it is known that the presence of a large number of extreme pressure additives in lubricating oil can lead to deterioration of their anti-corrosion properties. Thus, the author believes that when selecting the concentration of additives to transmission oils to take into account the corrosion-mechanical wear caused by the decomposition of the extreme pressure additive with increasing

temperature, it is necessary to evaluate the anti-wear properties [Oblaschikov, 2000]. It should also be noted that dithiophosphates, in addition to extreme pressure properties, also have anti-wear properties, which is also quite understandable. In recent years, articles have appeared on the mechanism of action of anti-wear additives, in particular, for phosphorus-containing additives. Thus, at moderate temperatures and physical loads, anti-wear additives, adsorbing on the metal surface, form thick polymer adsorption protective layers (Zakharchenko, 2005).

According to Yakunina K.A. the P=S bond at moderate loads is considered to be quite strong, the fragment adsorbing on the metal surface protects it from friction and wear. The author believes that dialkyldithiophosphates do not form phosphites or other phosphorus-containing compounds, they form a monomolecular protective layer consisting of dithiophosphates (Yakunina, 2022). So, in the area of moderate loads dithiophosphates show effective anti-wear properties and at high loads anti-seize properties.

1,3-(Bisisopropylxanthogenatosulfo)phenol, which differs from *p*-phenolsulfoisopropylxanthogenate by the presence of two xanthogen fragments, is well soluble in mineral oils, so the sample of experimental oil based on it was made in 5% concentration in MS-20 oil. Evaluation of lubricating properties showed high extreme pressure efficiency of the compound, which does not doubt the positive influence of the amount of sulfur in the molecule.

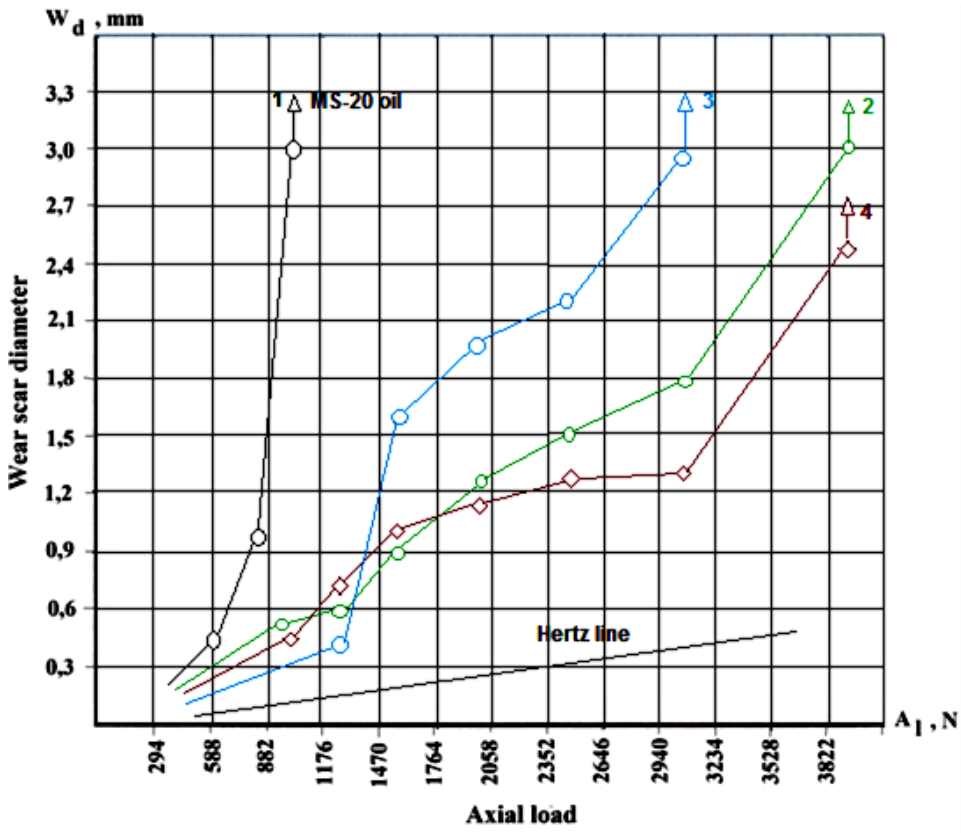


Figure 14. Extreme-pressure properties of MS-20 oil with synthesized compounds: 1 – MS-20 oil; 2 – p-toluenesulfonylbutyl xanthogenate (I) (5%); 3 – p-toluenesulfo diisopropyl dithiophosphate (III) (1.5%); 4 – 1,3-(bis-isopropyl xanthogenato sulfo)phenol (V)

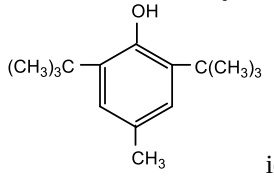
It should be noted that *p*-toluenesulphodiisopropyldithiophosphate compares favorably with arylsulfoxanthogenates in terms of seizure load (C_l) and wear spot diameter (W_d). However, it is inferior to xanthogen acid derivatives in terms of the seizure index (LW_I). This is explained by the fact that, due to the large amount of sulfur, 1,3-(bisizopropylxanthogenate)phenol and p-toluenesulfonylbutylxanthogenate provide milder seizure conditions than p-toluenesulfonylisopropyl dithiophosphate under high loads. It should be noted that 1,3-(bisizopropylxanthogenate)phenol has the highest extreme pressure properties. This is clearly illustrated in Figure 14, in the "wear-load" graph plotted in logarithmic coordinates.

As can be seen from the figure, the section characterizing the adhesion (limited by loads (C_l-W_l) on the curve for 1,3-(bis-isopropylxanthogenato)phenol is located closer to the Hertz line than on the curves for p-toluenesulfonyl butyl xanthate and *p*-toluenesulfonylisopropyl dithiophosphate, which shows its higher extreme pressiure properties.

4.2. Results of the study of antioxidant properties

Antioxidant properties of *p*-phenolsulfoisopropylxanthogenate (II) and 1,3-(bisisopropylxanthogenatosulfo)phenole (V), as well as the known antioxidant additive – ionol are presented (Table 5).

Table 5. Antioxidant properties of p-phenolsulfodiisopropylxanthogenate (II) and 1,3-(bisopropylxanthogenatosulfo)phenol (V)

Formula of compounds	at 60ºC		at 110ºC
	f	$K_7 \cdot 10^{-4}$ *l/mol·s*	τ, minute
II	2.30	2.83	230
V	2.40	2.50	200
2,6-ditretbutyl-4-methylphenol  ionol (for comparison)	2.0	2.10	150

The table shows that *p*-phenolsulfoisopropylxanthogenate (**II**) and 1,3-(bisizopropylxanthogenatosulfo)phenol (**V**) have antioxidant properties and according to the results obtained, surpass the well-known antioxidant additive to fuels and lubricants, ionol (Gershanov *et al*., 1995). The obtained results are quite correlated with the research data available in the literature.

It is known that in phenols screening by bulk substituents does not allow hydroxyl groups to form intermolecular hydrogen bonds. This is the reason for the choice of such structures as additives inhibiting the oxidation of hydrocarbons (Russkikh *et al*., 2013).

In order to study the reaction of these compounds with peroxide radic als, the initiated oxidation of cumene in their presence was studied (Figures 15, 16, 17, 18).

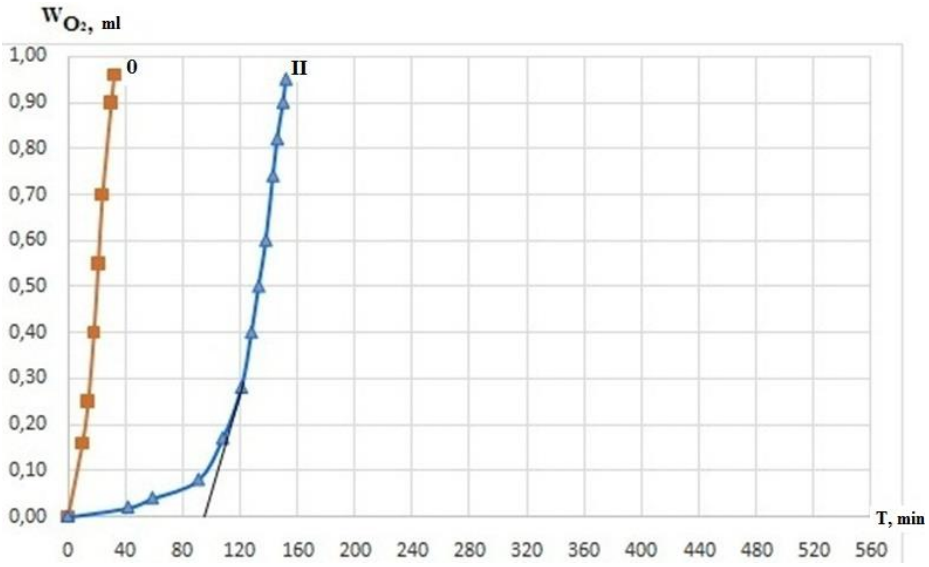


Figure 15. Kinetic curve of the initiated oxidation of cumene in the presence of p-Phenolsulfoisopropylxanthogenate (II) (60°C); [In·H]= $5 \cdot 10^{-4}$ *mol/l*; [AIBN] = $2 \cdot 10^{-2}$ mol/l (curve 0 without inhibitor)

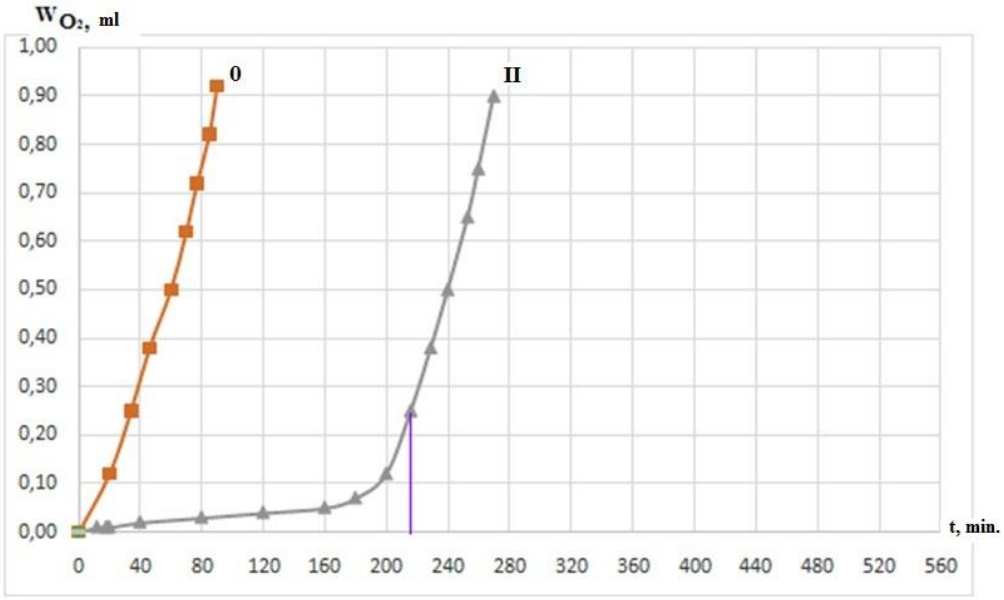


Figure 16. Kinetic curve of cumene autoxidation in the presence of p-Phenolsulfoisopropylxanthogenate (II) (T=110°C; [In·H]=$5 \cdot 10^{-5}$ mol/l (curve 0 without inhibitor)

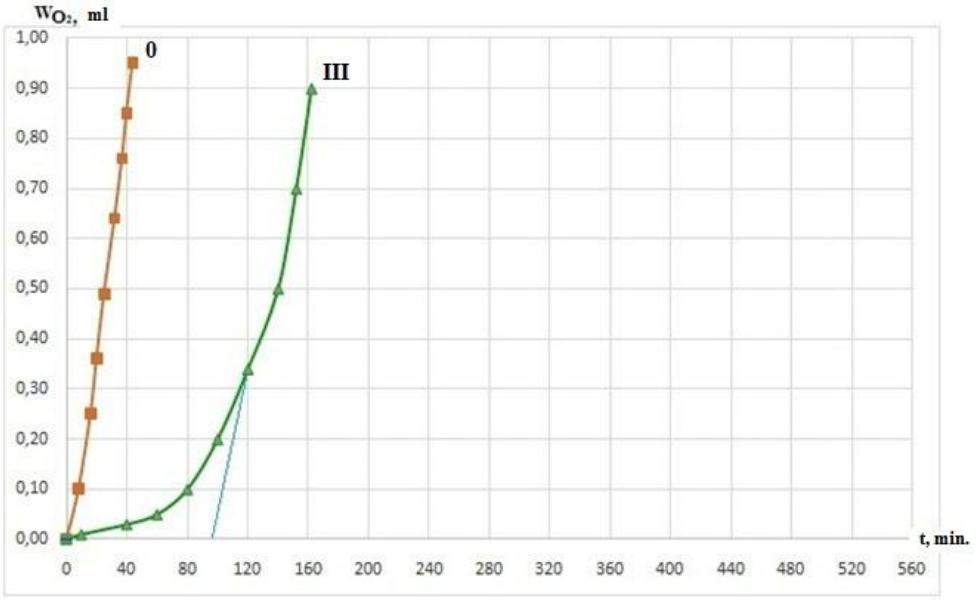


Figure 17. Kinetic curve of the initiated oxidation of cumene in the presence of 1,3-(bisisopropylxanthogenatosulfo)phenol (V) (60ºC.); [In·H]= $5 \cdot 10^{-4}$ mol/L; [AIBN] = $2 \cdot 10^{-2}$ mol/l (curve 0 without inhibitor)

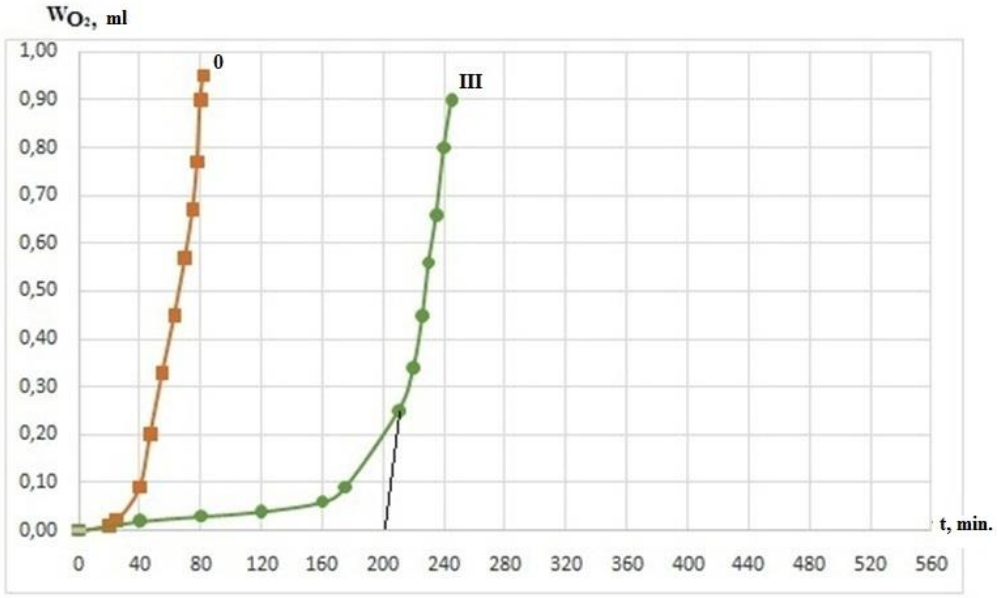


Figure 18. Kinetic curve of cumene autoxidation in the presence of 1,3-(bisisopropylxanthogenatosulfo)phenol (V) (T=110ºC; [In·H]=$5 \cdot 10^{-5}$ mol/L (curve 0 without inhibitor)

As follows from the data presented in Figures 15 and 16, the studied compounds effectively inhibit the oxidation process by reacting with cumene peroxide radicals.

The stoichiometric coefficient (τ) was calculated from the induction period $-f$, which is equal to the number of oxidation chains terminating on one inhibitor molecule and its transformation products:

$$f = \frac{\tau - W_i}{[I_n \cdot H]o}$$

where W_i – initiation rate equal to $2 \cdot 10^{-7}$ mol/(l-s), $[In \cdot H]_0$ – initial inhibitor concentration, mol/l.

To calculate the rate constant for the interaction of inhibitors with peroxide radicals –K_7, the oxygen uptake kinetic curves were transformed from $\Delta[O_2]$-t coordinates to $\Delta[O_2]$-t^1 coordinates and by the tangent of the slope angle equal to (Emmanuel *et al*., 1965; Denisov *et al*., 1985):

$$tga = \frac{f \cdot K_7 \cdot [I_n \cdot H]o}{K_2 \cdot [RH] \cdot W_i}$$

$$K_7 = \frac{tga \cdot K_2 \cdot [RH] \cdot W_i}{f \cdot [I_n \cdot H]o}$$

K_2 = 1.51 *l/mol·s*; [RH]=6.9 *mol/l*

The highest antioxidant properties are possessed by *p*-phenolsulfoisopropylxanthogenate (II) based on the data presented in Table 5 (*f*= 2.83, $K_7=2.6 \cdot 10^{-4}$ l/*mol·s*. Cumene oxidation induction period of 230 *min* and 1,3-(bisisisopropylxanthogenatosulfo)phenol (*f*= 2.40, $K_7=2.6 \cdot 10^{-4}$ *l/mol·s*). The induction period of cumene oxidation is 200 *min*, which is evident from the kinetic parameters.

5. Conclusion

The results of the analysis of physicochemical properties, elemental analysis and IR, NMR and chromato-mass spectrometry confirmed the production of derivatives of alkylxanthogen, diisopropyldithiophosphoric acids, as well as disulfide containing an arylsulfo group. Patents have been received for all synthesized compounds, which confirms their novelty.

It has been established that samples of oils prepared with the use of synthesized additives have increased extreme pressure properties and the highest extreme pressure properties are possessed by (bisphenylsulfo)disulfide, which containing –S–S–S–S bond, which easily breaks up under severe conditions of working of rubbing parts in oil environment.have been obtained for all synthesized compounds, which confirms their novelty.

It is shown that *p*-toluenesulfodiisopropyldithiophosphate along with extreme pressure properties also possesses anti-wear properties due to the strength of P=S bond adsorbed on the metal surface at moderate loads and temperature.

It was found that *p*-phenolsulfoisopropylxanthate and 1,3-(bisisopropylxanthate sulfo)phenol have not only anti-seize properties but also antioxidant properties due to the shielding of the hydroxyl group by bulky substituents.

Summarizing the results of the study, it can be stated that arylsulfate-containing compounds were first studied as additives to lubricating oils. Their advantage over many known additives is the availability of the starting reagents, most of which are commercial products.

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