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HIGH SULFUR COMPOUNDS AS ANTI-SEIZE ADDITIVES FOR TRANSMISSION OILS

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Abstract. In this work, the interaction of 2,2-dialkyl-4-chloromethyl-1,3-dioxolanes with sodium mono-, di- and trisulfides synthesized bis (2,2-dialkyl-1,3-dioxolan-4-yl-methylene)mono-, di- and trisulfides. It was revealed that the reactions to obtain sulfides proceed in an aqueous medium using tetrabutylammonium iodide as a catalyst $[(C_4H_9)_4N]J$.

Bis(2,2-dialkyl-4-methylene-1,3-dioxolane)trithiocarbonates were also synthesized by the interaction of 2,2-dialkyl-4-chloromethyl-1,3-dioxolanes with sodium trithiocarbonate. The 2,2-dialkyl-4-chloromethyl-1,3-dioxolanes used as starting reagents are synthesized on the basis of readily available and cheap glycerin, which is a by-product in the production of biodiesel fuel, which is currently in great demand. The structure of all synthesized compounds was proved by studying their physicochemical properties, including the determination of refractive indices(n_D^{20}), specific gravity(d_4^{20}) and the calculation on their basis of molecular refraction (MR_D calc. и MR_D found.) with their subsequent comparison, elemental composition and IR spectroscopy.

The anti-seize properties of the synthesized compounds were studied using a four-ball friction machine (FFM-1).

It was shown that all synthesized compounds have high anti-seize properties. The dependence of the efficiency of the lubricating properties of the synthesized compounds on their structure was revealed.

Keywords: *additive, anti-seize properties, dioxolan, disulfides, thitiocarbonate, transmission oils.*

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1. Introduction

At the present stage of development of mechanical engineering, lubricating oils are in great demand, depending on the requirements imposed on them, motor, transmission, industrial, synthetic, etc. oils are distinguished (Shkolnikov, 1999).

Transmission oils are intended for lubrication of gears of transmission units of various machines and mechanisms. The operation of oils in transmission units has some specific features. First of all, the conditions of friction in the contact of the teeth, where sliding and rolling occur, differ significantly from the conditions of friction in other mechanisms, they are distinguished by the long-term permanent operation of the oil poured into the transmission crankcase and an important feature – a wide range of operating temperatures (from 50°C to 150°C and above), in which the oil must remain fully functional.

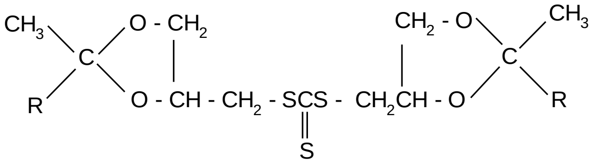
Transmission oils obtained by the distillation of petroleum products can only be used in mechanisms operating at low temperatures and light loads. In order to ensure the performance of transmission oils at high loads and temperatures, additives are added to their composition.

The practical goals of anti-seize additives are to improve the performance properties of oils, preventing the destruction of parts of gearboxes and other mechanisms.

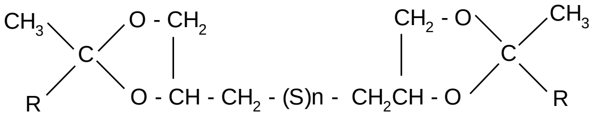
An important place among organic compounds of interest as anti-seize additives is occupied by compounds containing atoms of sulfur, nitrogen, phosphorus, chlorine and various functional groups (Khanov, 2003).

An important factor in the synthesis of oil additives is the use of readily available, cheap starting reagents (Farzaliyev, 2020; Mammadov, 2019).

We have synthesized a number of compounds based on glycerin derivatives and studied them as anti-seize additives. Including 1,3-dioxolane-tritiocarbonates were synthesized:



and 1,3-dioxolane mono-, di-, trisulfides:

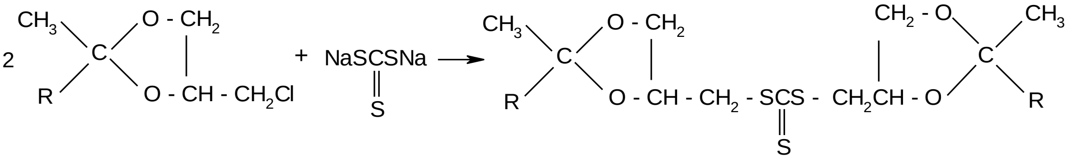


R=CH_3; C_4H_9

The main purpose of this work was to identify the anti-seize properties of sulfur-containing compounds of various structures.

2. Material and Methods

Bis(2,2-dialkyl-4-methylene-1,3-dioxolane)tritiocarbonates, obtained according to the scheme:



R=CH_3; C_4H_9

Syntesis of bis(2,2-dimethyl-4-methylene-1,3-dioxolane)tritiocarbonate

To 24 g (0.1 mol) of sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$) was fed 7.6 g (0.1 mol) of carbon disulfide (CS_2), the reaction mixture was stirred at 46°C for 1 hour. Then, 30 g (0.2 mol) of 2,2-dimethyl-4-chloromethyl-1,3-dioxolane, 2 g of tetrabutylammonium bromide $[(C_4H_9)_4N]Br$, taken as a catalyst, and 50 ml of petroleum ether were added to the reaction flask. The reaction was carried out for 7 hours at 70°C.

Bis(2,2-methyl-butyl-4-methylene-1,3-dioxolane)tritiocarbonate was prepared similarly.

Physicochemical parameters and elemental composition of the synthesized compounds:

Bis(2,2-dimethyl-4-methylene-1,3-dioxolane)tritiocarbonate

n_D^{20}– 1.5340; d_4^{20} – 1.1748; MR_D found. – 89.56; MR_D calc. – 90.48

$C_{13}O_4S_3H_{22}$: found, %: C – 46.00; S – 28.33; H – 6.40

Calculated, %: C – 46.12; S – 28.42; H – 6.55

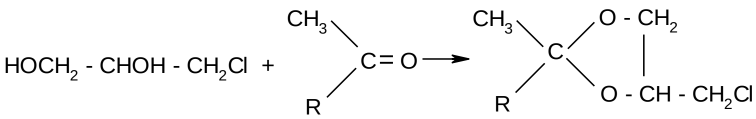
Bis(2,2-methyl-butyl-4-methylene-1,3-dioxolane)tritiocarbonate

n_D^{20}– 1.5210; d_4^{20} – 1.0960; MR_D found. – 117.4; MR_D calc. – 117.93

$C_{19}O_4S_3H_{34}$: found, %: C – 54.15; S – 22.67; H – 8.00

Calculated, %: C – 54.01; S – 22.76; H – 8.4

The starting 2,2-dialkyl-4-chloromethyl-1,3-dioxolane was obtained on the basis of glycerol and dimethyl ketone.



R=CH_3; C_4H_9

The reaction was carried out at a temperature of 30-32°C, in petroleum ether (f-35°C) for 14-15 hours (Mustafayev *et al.*, 2020; 1991; 2019).

Sodium tritiocarbonate was synthesized by the interaction of sodium sulfide with carbon disulfide.

$$Na_2S \cdot 9H_2O + CS_2 \longrightarrow NaSC(=S)SNa$$

The carbon disulfide used for the reaction was initially fed at room temperature and after stirring for 1 hour, the temperature was increased to 50°C, stirring was continued for another 1 hour.

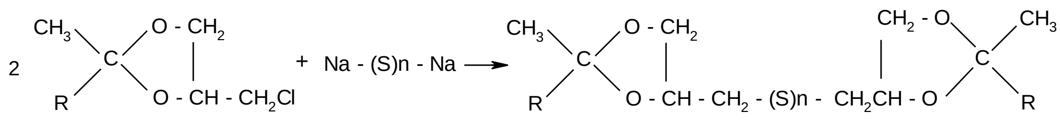
For the synthesis of bis(2,2-dimethyl-1,3-dioxolan-4-yl-methylene)mono-, di- and trisulfides, sodium mono-, di-, and trisulfides were synthesized as a starting reagent.

$$Na_2S \cdot 9H_2O + (S)n \longrightarrow Na - (S)n - Na$$

n=1,2,3

The reaction was carried out in an aqueous medium for 2 hours at a temperature of 65°C until the complete dissolution of sulfur. Then, without isolating sodium sulfides, the calculated amount of 2,2-dimethyl-4-chloromethyl-1,3-dioxolane and the catalyst tetrabutylammonium iodide were fed into the reaction flask. Stirring was continued at 75°C for 7 hours.

The reactions of sodium sulfides with 2,2-dimethyl-4-chloromethyl-1,3-dioxolanes proceeded according to the following scheme:



n=1,2,3
R=CH_3; C_4H_9

The composition and structure of the synthesized compounds have been proven by studying their physicochemical properties, elemental analysis, and IR spectroscopy.

3. Data and Methods

Separation and purification of the synthesized compounds was carried out by liquid column chromatography. Liquid column separation was carried out on an adsorption column with a length of 1.5 m and consisting of 3 sections with a diameter of 4 cm, 3 cm, and 1.5 cm. АСК (ГОСТ 3956-54) was used as an adsorbent. Separation on the column was monitored by thin layer chromatography (TLC) and the determination of refractive indices. TLC chromatography was performed on a loose layer (0.8 mm thick) of activity grade II alumina deposited on a 13x18 cm glass plate.

IR spectra were recorded on a SPECORD-75IR IR spectrophotometer from Carl Zeiss (GDR) using KBr, NaCl and Lif prisms in the range of 4000–100 cm^{-1}.

In the IR spectra of sulfides in the –S–S– fragment, absorption bands in the range of 490±10 cm^{-1} are identified, characterizing the C–O bond at 1088-1066 cm^{-1}, the absorption bands of C–H bonds are observed in the range of 2098.77-2955, 2872 cm^{-1}.

The identification of thiocarbonyl absorption in the IR spectra of tritiocarbonates presents no difficulty.

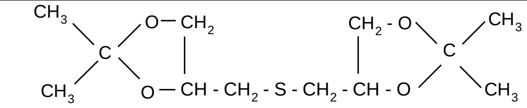
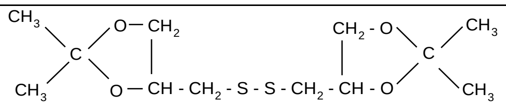
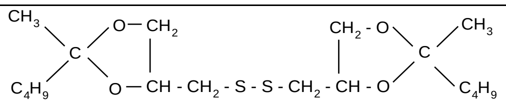
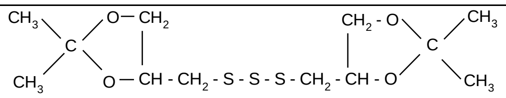
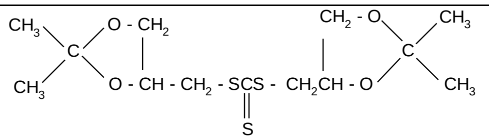
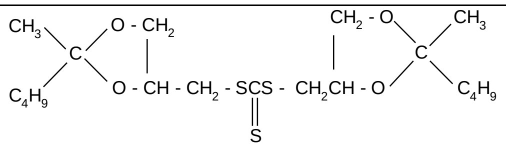
According to Bellamy, C=S bonds in tritiocarbonates are characterized by a strong band in the frequency range 1100-1050 cm^{-1} (Bellamy, 1958). In the IR spectrum of bis(2,2-dimethyl-4-methylene-1,3-dioxolane)tritiocarbonate, the absorption band in the range of 1059.82 cm^{-1} is due to stretching vibrations of the C=S group, frequencies in the range of 792.47 cm^{-1} correspond to the C–S bond, the band at 1259.93 cm^{-1} refers to the vibrations of the –C–O–C– group.

Extreme pressure properties were determined by the ASTM D2596 test method, the estimated indicators were the scuffing index, the critical load, the welding load.

4. Application and Results

The synthesized compounds were tested in 5% concentration in AK-15 gear oil as extreme pressure additives. As shown by the research results, both 1,3-dioxolane disulfides and 1,3-dioxolane-tritiocarbonates have high anti-seize properties and can be used as additives for transmission oils.

Table 1. Extreme pressure properties of bis(2,2-dimethyl-1,3-dioxolan-4-yl-methylene)trisulfides and bis(2,2-methylbutyl-4-methylene-1,3-dioxolan)tritiocarbonate

Compounds	Concen-tration of samples in oil, %	Extreme pressure properties acc. to ASTM D2596		
		Scuffing index, N	Critical load, N	Welding load, N
	5	411	980	1586
	5	528	980	3980
	5	450	980	3096
	5	714	1235	4410
	5	519	1235	3980
	5	519	1098	3097
AK-15 transmission oil	–	326	686	980

5. Results and discussion

With the interaction of 2,2-dialkyl-4-chloromethyl-1,3-dioxolanes with sodium mono, di- and trisulfides and sodium tritiocarbonate, bis (2,2-dialkyl-1,3-dioxolan-4-yl-methylene)mono-, di-, trisulfides and bis(2,2-dialkyl-4-methylene-1,3-dioxolane)tritio-carbonates, respectively were synthesized.

The results of studies of tribological properties show that both in the series of sulfides and in the series of tritiocarbonates, the anti-seize properties decrease with the elongation of the alkyl radicals. This is explained by the fact that the larger the alkyl radical, the lower the probability of compact adsorption on the metal surface, that is, the adsorbed sulfur forming a sulfide protective layer with the metal surface will be much less than in the case of more compact adsorption of compounds with short radicals.

Comparison of the values of the characteristic parameters, which can be used to judge the lubricating properties of sulfides, shows that with the lengthening of the chain of sulfur atoms, the extreme pressure efficiency increases. This is explained by the easy cleavage of the –S–S–, bond, which leads to the formation of a protective layer of iron sulfides on the metal surface (Sangalov *et al.*, 2004). It should also be noted that, despite the high extreme pressure efficiency of 1,3-dioxolane tritiocarbonates, their lubricating properties are close to disulfides, since tritiocarbonates also contain 2 sulfide sulfur atoms, however, they are inferior to trisulfides in the indicated properties.

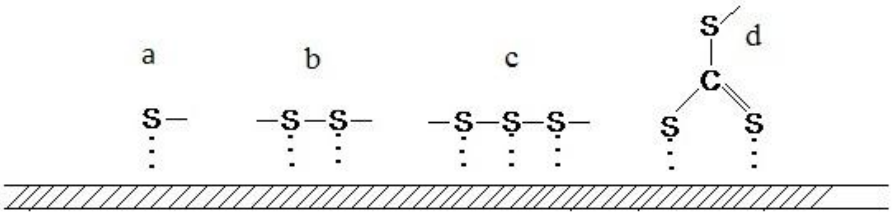


Fig.1. Adsorption of molecules of synthesized compounds: a) monosulfide; b) disulfide; c) trisulfide; d) tritiocarbonate

Although trisulfide and tritiocarbonate each contain three sulfur atoms, according to the geometry of the considered molecules in tritiocarbonate, only two heteroatoms out of three can simultaneously participate in the formation of a bond with the surface, while in trisulfide all three sulfur atoms participate in the formation of a protective layer, which is consistent with the data obtained when determining the extreme pressure properties of the compounds.

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