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UNSYMMETRICAL DISULPHIDES AS ADDITIVES TO TRANSMISSION OILS

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Abstract: *This paper presents the results of studies of the anti-seize properties of (2,2-dimethyl-4-methylene-1,3-dioxolane-allyl and benzyl)disulfides synthesized on the basis of 2,2-dimethyl-4-chloromethyl-1,3-dioxolane, sodium disulfide and allyl and benzyl chlorides, respectively, in the composition of transmission oils. The synthesized compounds are new compounds not previously described in the literature, the structure of which has been proven by studying their physicochemical properties, elemental composition, and IR spectroscopy. It revealed that the synthesized compounds in terms of extreme pressure efficiency are significantly superior to transmission oil MS-20, as well as bis(2,2-dimethyl-4-methyl-1,3-dioxolane)disulfide, previously synthesized by the authors of this article and a typical extreme pressure additive ethylene-bis-isopropylxanthate (LZ-23k). It found that the replacement of one of the 1,3-diocosolane fragment in bis(2,2-dimethyl-4-methylene-1,3-dioxolane) disulfide with allyl or benzyl radicals leads to an improvement in anti-seize properties due to their better adsorption on metal surfaces of rubbing parts.*
Keywords: *disulfide, 1,3-dioxolane, anti-seize properties, transmission oils, additive.*
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Introduction

The growth trend in the automotive industry causes an increase in demand for effective additives to lubricating oils, which ensure the creation of high-quality lubricating oils that reduce friction and wear of machine parts and mechanisms for their intended purpose.

Transmission oils are used to lubricate gearboxes, steering gears, gears and chains of all types, and in this work, new compounds are proposed as oil additives, on the basis of which high-quality transmission oils can be created.

It should be noted that when creating high-quality oils, the creation of additives from available and cheap raw materials is of no small importance. Such is glycerin, which as a plug product is formed in the production of biodiesel [2].

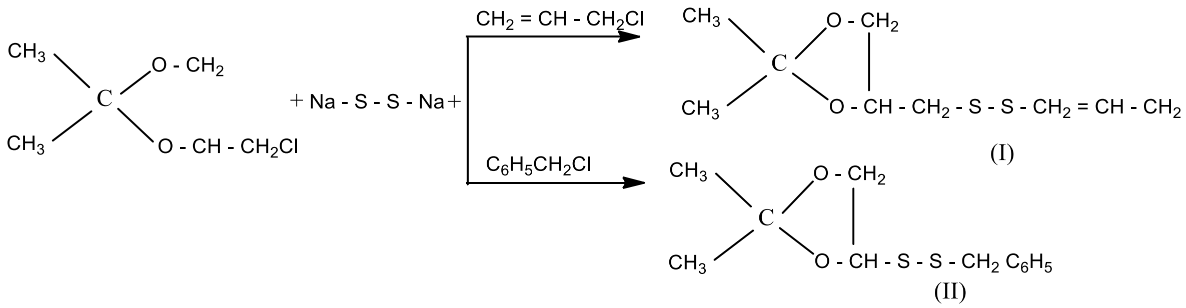
Based on this cheap raw material, compounds used in numerous areas of the national economy have been synthesized. Of the derivatives of glycerol, 1,3-dioxolanes are especially widely used, which are quite easily obtained by the interaction of glycerol and ketones [3, 4]. And although a large number of compounds used for practical purposes have been obtained on their basis, however, information on their use as additives to lubricating oils is almost absent [5-7].

The main goal of the work was the synthesis of new unsymmetrical disulfides based on 1,3-dioxolanes and the study of the influence of the structure of the fragments that make up the compounds on their anti-seize properties.

Experimental part

Based on 1,3-dioxolane, we synthesized (2,2-dimethyl-4-methylene-1,3-dioxolane-allyl)disulfide and (2,2-dimethyl-4-methylene-1,3-dioxolane-benzyl)disulfide.

The proposed disulfides were synthesized according to the following scheme:

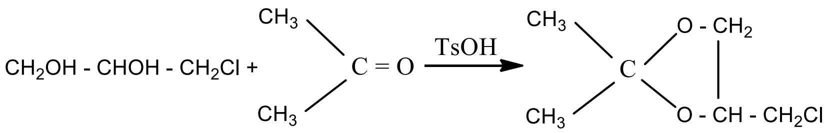


At the first stage of the work, α-chloropropanediol was synthesized by saturation of glycerol with dry hydrogen chloride:

$$CH_2OH - CHOH - CH_2OH + HCl \longrightarrow CH_2OH - CHOH - CH_2Cl$$

(n_D^{20}) – 1.4784; (d_4^{20}) – 1.3146; MR_D found. – 22.31; MR_D calc. – 22.37

With the subsequent interaction of which with dimethyl ketone, 2,2-dimethyl-4-chloromethylene-1,3-dioxolane was obtained:



(n_D^{20}) – 1.4350; (d_4^{20}) – 1.0937; MR_D found. – 35.80; MR_D calc. – 35.86

Sodium disulfide was obtained by dissolving sulfur in sodium sulfide nonahydrate:

$$Na_2S \cdot 9H_2O + S \xrightarrow{70^0C} Na - S - S - Na$$

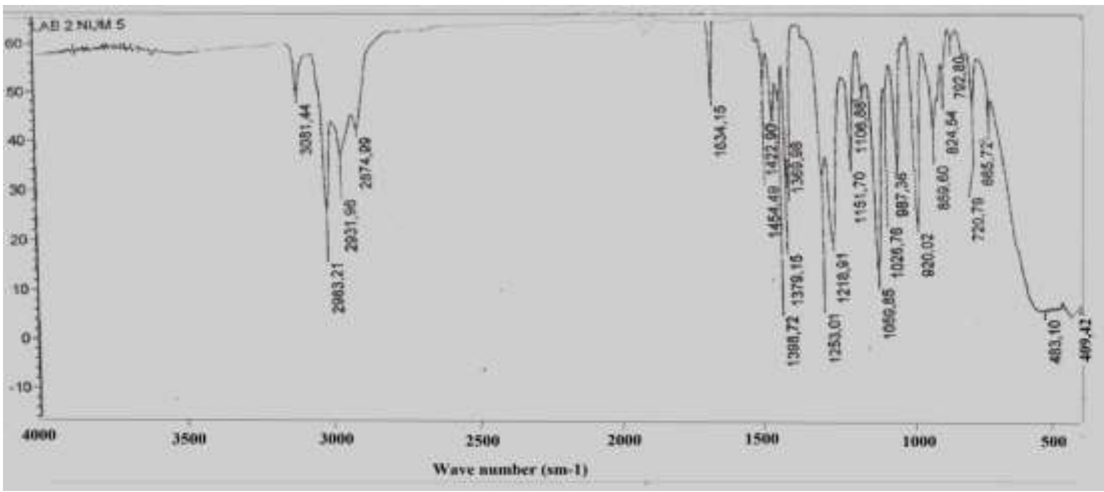


Fig. 1. Infrared spectrum (2,2-dimethyl-4-methylene-1,3-dioxolane-allyl)disulfide

The individuality of the obtained compounds was proved through determining their elemental composition (C, S, N, H, Cl) by the TruSpec-Micro (LECO) analyzer, refractive indices (n_D^{20}), specific gravity (d_4^{20}) with calculations of MR_D found. and MR_D calc., as well as IR spectroscopy. IR spectra were taken on a SPECORD-75IR IR spectrophotometer, Carl-Zeiss (Germany) using KBr prisms in the region – 4000-400 cm^1.

In the IR spectrum of (2,2-dimethyl-4-methylene-1,3-dioxolane-allyl)disulfide (Fig.1) –S–S– absorption bands in the region of 483±10 cm^{-1} were identified, characterizing the –C=S– bond 1634 cm^{-1}, absorption bands =C–H bonds are observed in the region of 3081 cm^{-1}, bands above 3000 indicate the presence of an unsaturated bond, bending vibrations of $\delta_{C\text{–}H}$ correspond to 920-859 cm^{-1} [8].

In the IR spectrum of (2,2-dimethyl-4-methylene-1,3-dioxolane-benzyl)disulfide (Fig.2) absorption bands of the C-H bond are observed in the aromatic 3093,89-1634 cm^{-1}, 3060,80-1634 cm^{-1}, 3027-1634 cm^{-1}, absorption bands correspond to the aromatic ring 1300,73-1634 cm^{-1}, 1583-1634 cm^{-1}, 1538-1634 cm^{-1}, 1494-1634 cm^{-1}, 1453-1634 cm^{-1}, bending vibrations $\delta_{C\text{–}H}$ correspond to 697 cm^{-1}, 763 cm^{-1}, 862 cm^{-1}, 913 cm^{-1}.

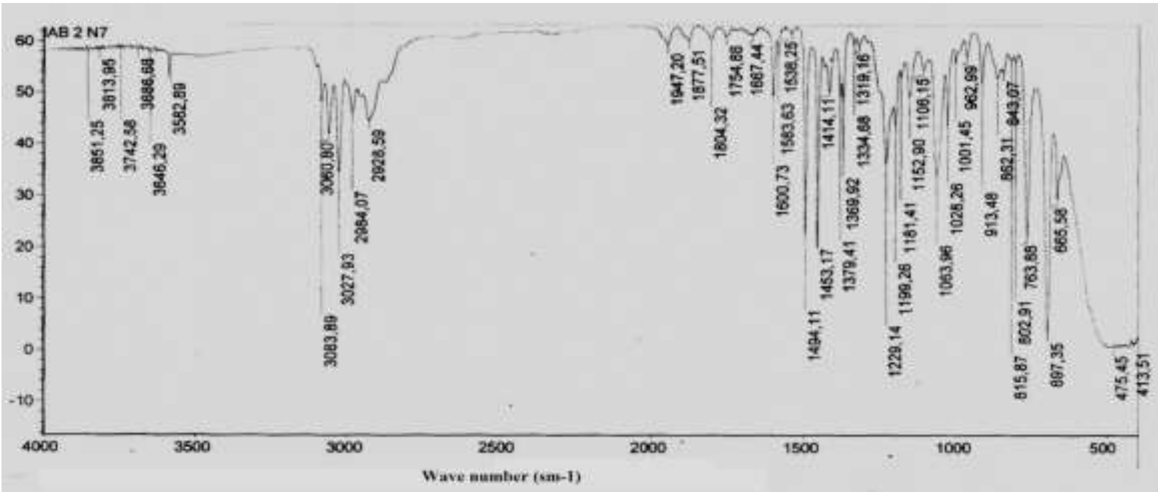


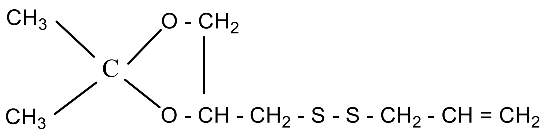
Fig. 2. Infrared spectrum (2,2-dimethyl-4-methylene-1,3-dioxolane-benzyl)disulfide

Anti-seize properties were determined by the ASTM D2596 test method, the estimated indices were the load wear index, the critical load, the welding load.

Syntheses of disulfides were carried out as follows:

The installation used in the production of disulfides consists of a glass three-necked flask equipped with a thermometer and a dropping funnel and a mechanical stirrer heated by an electric mantle heater.

(2,2-Dimethyl-4-methylene-1,3-dioxolane-allyl)disulfide (I) is as follows:



24 g (0.1 mol nanohydrate) of sodium sulfide ($Na_2S\cdot 9H_2O$), 3.2 g (0.1 mol) of sulfur (S) and 50 ml of water were placed in a reaction flask, stirred at 70°C for 1 hour, then in the flask was fed with 15 g (0.1 mol) of 2,2-dimethyl-4-chloromethyl-1,3-dioxolane and 0.6 g of tetrabutylammonium bromide $[(C_4H_9)_4N]Br$ as a catalyst, 50 ml of benzene and stirred for 30

minutes, allylchloride was added to the flask, stirring was continued for 4 hours at 60-65°C.

The resulting product was washed with water; benzene was distilled off and dried under vacuum. The yield of the obtained product is 17 g (77.3%).

Physical and chemical characteristics and elemental composition of the product are as follows:

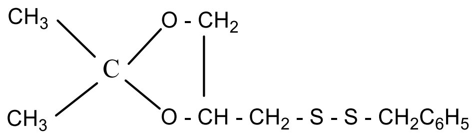
(n_D^{20}) – 1.4990; (d_4^{20}) – 1.1190; MR_D found – 58.65; MR_D calc. – 58.09

$C_8H_{16}O_2S_2$: found, %: C – 48.95; H – 7.00; S – 29.1

Calculated, %: C – 49.06; H – 7.32; S – 28.92

(2,2-Dimethyl-4-methylene-1,3-dioxolane-allyl)disulfide, brown liquid, soluble in solvents and mineral oils.

(2,2-dimethyl-4-methylene-1,3-dioxolane-benzyl)disulfide (II) is as follows:



In a reaction flask at 70^{0}C, 24 g (0.1 mol) of sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$), 3.2 g (0.1 mol) of sulfur and 50 ml of water were stirred for 1 hour, then 15 g (0.1 mol) of 2,2-dimethyl-4-chloromethylene-1,3-dioxolane was added, 50 ml of benzene and 0.6 g of tetrabutylammonium bromide $[(C_4H_9)_4N]Br$ as a catalyst were stirred for 40 minutes. Then, 8.7 g (0.1 mol) of benzylchloride was added to the flask and stirring was continued for 5 hours. The product was washed with water; benzene was distilled off and dried under vacuum. The yield of the obtained product is 14 g (72%).

Physical and chemical characteristics and elemental composition of the product are as follows:

(n_D^{20}) – 1.5290; (d_4^{20}) – 1.0954; MR_D found. – 76.1; MR_D calc. – 75.52

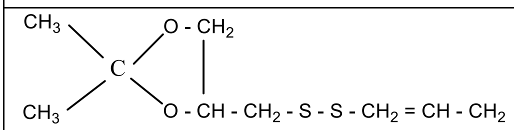
$C_{13}H_{18}O_2S_2$: found, %: C – 57.84; H – 6.81; S – 23.49

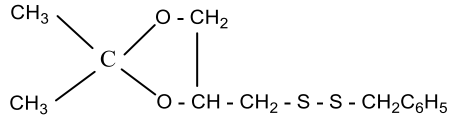
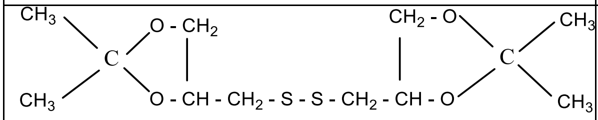
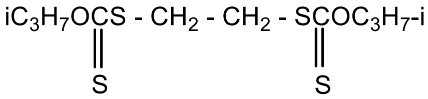
Calculated, %: C – 57.9; H – 6.69; S – 23.63

The synthesized compounds were tested at 5% concentration as anti-seize additives in MC-20 gear oil.

To determine the effectiveness of the synthesized disulfides, Table also provides data on the anti-seize properties of bis(2,2-dimethyl-4-methylene-1,3-dioxolane) disulfide previously synthesized by the authors, as well as the well-known typical anti-seize pressure additive LZ-23к (ethylene-bis-isopropylxanthate) (ГОСТ 11883-77).

Table 1. Tribological characteristics of the synthesized compounds in MC-20 gear oil

Compounds	Concentration of samples in oil, %	Extreme pressure properties ass. to ASTM D2596		
		Load wear index, N	Critical load, N	Welding load, N
 (I)	5	720	1098	3920

 (II)	5	731	980	4381
	5	528	980	3980
	5	528	980	3980
MC-20 oil	–	330	794	1568

Results and discussion

It should be noted that, in general, all disulfides are characterized by high extreme pressure properties caused by the fact that the –S–S– bond is relatively easily broken and a protective layer consisting of iron sulfides (FeS, Fe_2S_3) is formed on the metal surface [9, 10].

The test results showed that the disulfides synthesized by the authors of this work also have high anti-seize properties, and disulfides containing allyl and benzyl fragments, in these properties, are somewhat superior to the known bis (2,2-dimethyl-4-methylene-1,3-dioxolane) disulfide and a typical anti-seize additive LZ-23k.

The higher anti-seize properties of the proposed disulfides compared with the structure of bis(2,2-dimethyl-4-methylene-1,3-dioxolane) disulfide can be explained by the presence in the bis(2,2-dimethyl-4-methylene-1,3-dioxolane) disulfide of 2 dioxolane fragments, which are somewhat more difficult to adsorb on the metal surface due to their branched structure. And the replacement of one of the dioxolane fragments with allylic or benzyl radicals significantly increases the adsorption of the compound on the metal surface, which leads to accelerated formation of a protective layer that reduces the surface destruction of rubbing parts [11].

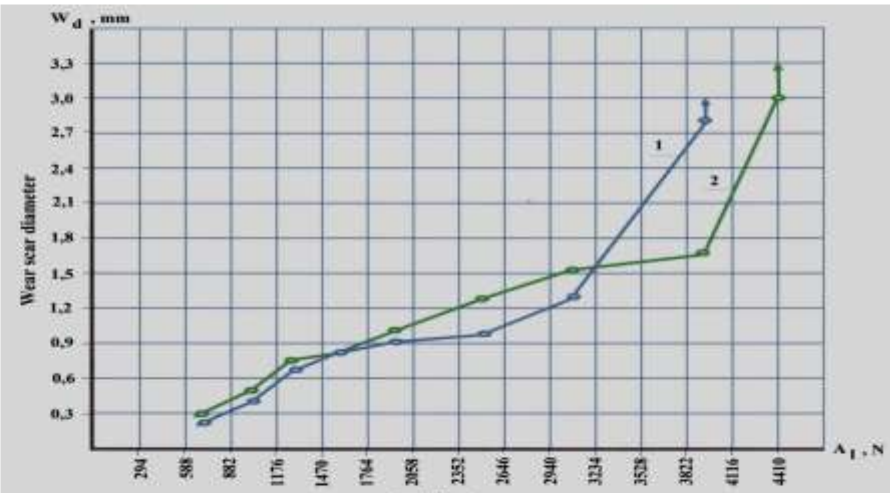


Fig. 3. "Wear-load"graph in lagorithmic coordinates: 1) (2,2-Dimethyl-4-methylene-1,3-dioxolane-allyl)disulfide; 2) (2,2-dimethyl-4-methylene-1,3-dioxolane-benzyl)disulfide

A comparison of the anti-seize properties of the synthesized disulfides with each other showed that the critical loads of both compounds are very close in their values, however, in terms of the welding load and the load wear index, (2,2-dimethyl-4-methylene-1,3-dioxolane-benzyl)disulfide is somewhat superior according to this parameter (2,2-dimethyl-4-methylene-1,3-dioxolane-allyl)disulfide, which can be clearly seen in the figure 3.

The curves clearly show changes in wear scar diameters (Wd) of joints 1 and 2 with load.

The higher anti-seize properties of (2,2-dimethyl-4-methylene-1,3-dioxolane-benzyl)disulfide can be explained as being due to its low thermal stability, as is known that the lower the thermal stability of the compounds, the higher their anti-seize properties.

Thus, the synthesized disulfides obtained on the basis of readily available and cheap raw materials – glycerol, have sufficiently high extreme pressure properties, following which these compounds may be of interest as extreme pressure additives for transmission oils used in gearboxes and other mechanisms.

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ASİMMETRİK DİSULFİDLƏR TRANSMİSSİYA YAĞLARINA AŞQAR KİMİ

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Xülasə: Bu işdə müvafiq olaraq 2,2-dimetil-4-xlorometil-1,3-dioksolan, natriium disulfidvə allil-, benzilxloridlər əsasında sintez edilən (2,2-dimetil-4-metilen-1,3-dioksolan-alil və benzil)disulfidlərin transmissiya yağları tərkibində siyrilməyə qarşı xüsusiyyətlərinin tədqiqat nəticələri təqdim olunur. Sintez edilmiş birləşmələr əvvəllər ədəbiyyatda təsvir olunmayan, strukturu fiziki-kimyəvi xassələri, element tərkibi və İQ-spektroskopiyasının öyrənilməsi ilə sübut edilmiş yeni birləşmələrdir. Sintez edilmiş birləşmələrin siyrilməyə qarşı xassələri ЧМТ-1 dörd kürəli sürtünmə maşınında təyin edilmişdir. Müəyyən edilmişdir ki, sintez edilmiş birləşmələrin siyrilməyə qarşı xassələri MS-20 transmissiya yağından, həmçinin əvvəllər bu məqalənin müəllifləri tərəfindən sintez edilmiş bis(2,2-dimetil-4-metil-1,3-dioksolan)disulfid və müqayisə üçün götürülmüş tipik etilen-bis -izopropil ksantogenatdan (ЛЗ-23k) xeyli üstündür. Təqdim olunmuş işdə əsas triboloji xassələrin öyrənilməsi zamanı, 4-kürəli sürtünmə maşınında şarların yeyilmə izinin diametrinin necə dəyişildiyi aydın görünür (şəkil 3). Müəyyən edilmişdir ki, bis(2,2-dimetil-4-metilen-1,3-dioksolan) disulfidin tərkibindəki 1,3-diokosolandan birinin allil və ya benzil radikalları ilə əvəz edilməsi onların siyrilmə xassələrini yaxşılaşdırır, bunu onunla izah etmək olar ki, metal səthlərdə daha yaxşı adsorbsiya olunur.
Açar sözlər: disulfid, 1,3-dioksolan, siyrilmə xassələri, transmissiya yağları, aşqar

НЕСИММЕТРИЧНЫЕ ДИСУЛЬФИДЫ В КАЧЕСТВЕ ПРИСАДОК К ТРАНСМИССИОННЫМ МАСЛАМ

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Аннотация: В работе представлены результаты исследований противозадирных свойств (2,2-диметил-4-метилен-1,3-диоксолан-аллил и бензил)дисульфидов, синтезированных на основе 2,2-диметил-4-хлорметил-1,3-диоксолана, дисульфида натрия и аллил- и бензилхлоридов, в составе трансмиссионных масел. Синтезированные соединения представляют собой новые ранее неописанные в литературе соединения, структура которых доказана исследованием их физико-химических свойств, элементного состава и ИК-спектроскопией. Установлено, что синтезированные соединения по противозадирной эффективности значительно превосходят трансмиссионное масло МС-20, а также бис(2,2-диметил-4-метил-1,3-диоксолан)дисульфид, ранее синтезированный авторами настоящей статьи и типичную противозадирную присадку этилен-бис-изопропилксантогенат (ЛЗ-23к). Показано, что замена одного из 2-х диоксолановых фрагментов в бис(2,2-диметил-4-метилен-1,3-диоксолан)дисульфиде на аллильный или бензильный радикалы приводит к улучшению противозадирных свойств, ввиду их лучшей адсорбции на металлической поверхности трущихся деталей.
Ключевые слова: дисульфид, 1,3-диоксолан, противозадирные свойства, трансмиссионные масла, присадка.