

Synthesis and structure of sulfur-containing antifriction additives for lubricants

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The resource and energy saving, environmentally friendly method of obtaining of extreme pressure additives for lubricants, that is differed from the known by improved technical and economic parameters of fatty esters sulfurization with elemental sulfur was developed. The structure and structural peculiarities of the obtained products were determined by IR-spectrometry and differential scanning calorimetry.

In the field of lubricants the sulfur-containing hydrocarbons, especially olefins, vegetable oils and their esters play a key role. These compounds contain sulfur in 0, -1 oxidation state bound either to carbon or sulfur atoms forming tribo-active mono-, di- and polysulfide groups that provide high antifriction and antiwear characteristics of lubricants of various purpose at low concentrations. Except excellent lubricating properties they are ecologically friendly for the environment and in contrast to commonly used additives such as chlorinated paraffin and derivatives of heavy metals, subjected to biodegradation without formation of toxic substances [1].

The production of sulfur-containing additives for lubricants began in the first half of the last century and constantly increases for nowadays with the development of modern technology, operating at high speeds and loads. In scientific and technical literature there are a growing number of publications devoted to the synthesis of new sulfur carriers. They differ in methods of synthesis, chemical structure and composition, nature and origin of the initial reagents [1–14]. The different types of alkenes [2–4], especially α -olefins with different length of hydrocarbon chain (C_6 – C_{30}) [3] and terpenes [4], alkylphenols [5], synthetic alcohols [6] and acids [7] and their esters [8], acrylates and salicylates [9], oils and animal fats [7, 10, 11] and their esters [12–14], also various compositions based on these reagents [3, 14] are the main raw material in the production of sulfur carriers.

Being aware of fossil organic material fund exhaustion, high cost and environmental disadvantages of mineral-based products, using renewable plant material, especially oils and their esters is a more rational in our opinion. The choice of oils or esters is outstanding. Oils have better lubricating properties [1], but lower thermal-oxidative stability, because of relatively easy oxidation of β -ester carbon atom in the molecule of triglycerides. Sulfurization of oils occurs at high temperature namely 180–200 °C for 1,5–2,5 hours and additional input of reaction activators. In such circumstances as a result of cross-linking of triglycerides molecules and the formation of solid factice- structures it is

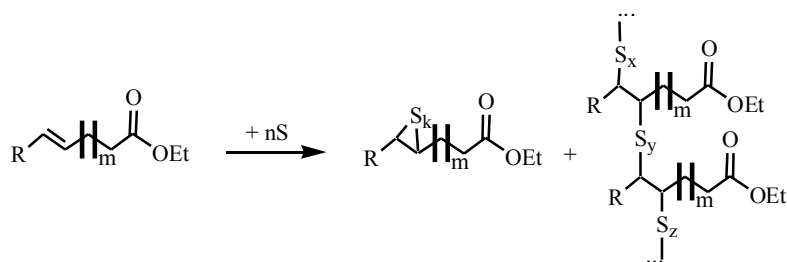
possible to bind chemically not more than 25 wt. % of sulfur, that makes impossible to use them [10].

Oils esters obtain the transesterification with low molecular alcohols (alcoholysis). Upon methanolysis, a mixture of higher fatty acid methyl esters (FAME) as “biodiesel” well-known commercial product. The prospects for increasing of production volume of this fuel in Ukraine are attractive and desirable for economic and political realities, and also due to the actual environment situation, since the lubricating ability of biodiesel is contributed to a longer life of the nozzles and increased the overhaul life of the engine for almost 50 %, while reduced toxic oxides of carbon and nitrogen.

However, in opposition to the positives of methyl esters as a fuel their exploitation in lubricants is problematic in terms of environmental concerns due to the using of toxic methanol and creation of high hazard in the production and application of FAME.

According to the known methods of sulfurization, not more than 28 wt. % sulfur in the presence of 0,5–1,0 wt. % activators, such as 2-thiobenzothiazole, polyethylenepolyamine and their mixtures, or in the case of crude esters – 0,1–1,0 wt. % activators-corrosion inhibitors: azimido-benzene, high-alkali calcium alkylsalicylate, etc. may be introduced in the molecules of methyl esters of oil acids [12]. In the patent [13] a mixture of methyl esters and elemental sulfur is heated in three stages: up to 160–165 °C, then slowly up to 175–180 °C for 30–45 min and 30–45 min of holding in addition. In both methods the sulfurization process is completed at 170–180 °C and accompanied by releasing of hydrogen sulfide into environment.

Regardless on the fact, that sulfur carriers are used in lubricants for about 100 years, the discussion about the structure and properties of the products depending on the conditions of synthesis is carried out till now. The differences in the structure of the products obtained from various raw materials by counter methods are reported, the mechanisms of reactions, involving parallel formation of by-products are proposed [1, 14–16]. The dark color of sulfurization products, also, is remained unsolved.



R – hydrocarbon chain; Et – C₂H₅; n = 1–46 wt. %; k = n – (x + y + z); m = 7–13

Scheme 1.

The development of the method of producing of sulfurized additives for lubricants, based on renewable ecofriendly natural raw materials and the study of their structure and properties depending on the process conditions, ratio of initial reagents, sulfur content are the aims of our work.

Experimental

We solved the problem by sulfurization of higher fatty acid ethyl esters (FAEE) of rapeseed and sunflower oils with elemental sulfur as follows [17] (Scheme 1).

For this purpose FAEE mixed with elemental sulfur in calculated quantities. The resulting reaction mixture was heated to 130–150 °C for 10–20 min, then the temperature was raised to 160–165 °C and maintained under these conditions about 20–30 minutes depending on the composition of the starting materials. As a result, we received sulfurized FAEE (Eterol–S_n) with a content of chemically bound sulfur (n = 1–46 wt.%). The course of reaction was monitored by the change of free sulfur concentration in the system. Sulfur, unlike sulfur carriers, is poorly soluble in hydrocar-

bons, so the samples were taken and dissolved in heptane during reaction. The moment when sulfur is not crystallized from solution upon cooling is taken as the time of the end of reaction. The mixture is kept under established optimal conditions for 5–10 minutes before total closure of the process.

The ratio of the reagents, conditions and results of synthetic studies are summarized in Table.

The determination of structure and composition of sulfurized products are studied by IR–spectrometry and differential scanning calorimetry (DSC) and other properties are determined by conventional standard methods.

Results and discussion

Analysis of the obtained synthesis results, summarized in Table, shows that the use of FAEE the conditions of sulfurization compared to the same process for rapeseed oil [10] or FAME [12–13] based on it are greatly alleviated. Thus, the process temperature is decreased from 180–200 °C for oil (sample 1) and 175–180 °C for esters (sample 2) to 160–165 °C (samples 3–8) with reducing the duration of

Conditions and results of the synthesis of sulfur-containing esters of higher fatty acids

№	Initial reagents and conditions of sulfurization					Results of synthesis			
	Reagent		S Quantity, wt. %	Temperature, °C	Duration, min	Yield, wt. %	S Content, wt. %	Viscosity, mm ² /s (40 °C)	Iodine value, g I ₂ / 100 g
	Name	Quantity, wt. %							
1	Rapeseed oil	92,0	8,0	160–175 180–200	20–40 60–110	93	7,4	305,2	–
2	FAME	87,0	13,0	160–165 175–180	10–20 30–45 30–45	95	12,4	43,13	–
3	FAEE	95,0	5,0	130–150 160–165	10–20 20–30	100	5,0	8,46	53,36
4	FAEE	90,0	10,0	130–150 160–165	10–20 20–30	99	9,9	14,56	48,83
5	FAEE	85,0	15,0	130–150 160–165	10–20 20–30	98	14,7	39,34	47,61
6	FAEE	80,0	20,0	130–150 160–165	10–20 20–30	98	19,8	55,9	47,06
7	FAEE	70,0	30,0	130–150 160–165	10–20 20–30	97	29,1	93,87	46,44
8	FAEE	60,0	40,0	130–150 160–165	10–20 20–30	96	38,4	158,49	45,55
9	FAEE	50,0	50,0	130–150 160–165	10–20 20–30	91	45,7	281,83	44,79

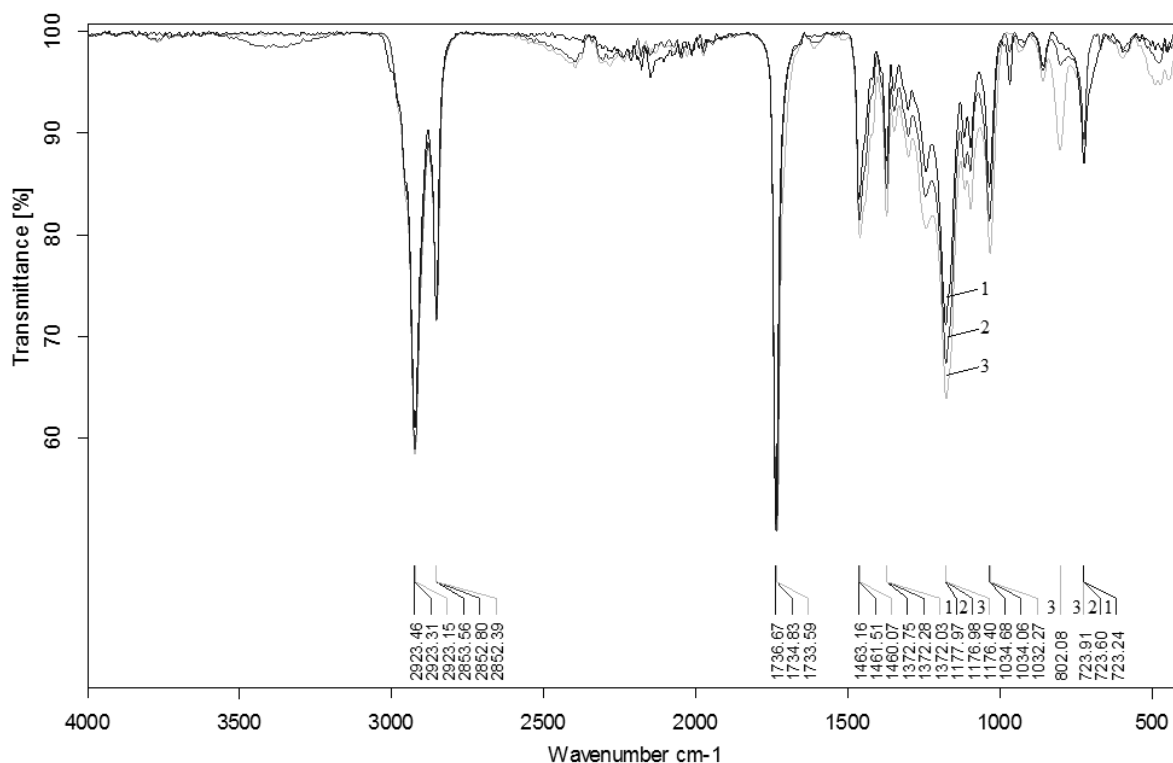


Figure 1. IR-spectra of sulfurized fatty acid ethyl esters with sulfur content, wt. %: 1 – 5; 2 – 19,8; 3 – 38,4

the reaction for 50–100 min and 40–60 min, respectively.

IR-spectra analysis of initial rapeseed oil and ethyl esters clearly indicates the presence of stretching vibration of C=O group at 1740 cm^{-1} and C–O at $1190\text{--}1160\text{ cm}^{-1}$ that distinctive for esters structure $\text{C}(\text{O})\text{OR}$, and the broad low intensity band in the range of $3650\text{--}3200\text{ cm}^{-1}$ corresponding to hydrogen bonds [18, 19]. There are also stretching vibrations of --CH_2 groups at $2985\text{--}2850\text{ cm}^{-1}$, pender vibrations of methylene groups $\text{--}(\text{CH}_2)_m\text{--}$ ($m > 4$) at 720 cm^{-1} and deformation vibrations of --C--H groups, including: asymmetric --CH_3 ($1430\text{--}1410\text{ cm}^{-1}$), symmetric --CH_3 ($1380\text{--}1370\text{ cm}^{-1}$) and internal deformation vibrations --CH_2 ($1485\text{--}1445\text{ cm}^{-1}$), typical for groups in long hydrocarbon chains. Also weak intensity bands at 3020 cm^{-1} and in the region of $1005\text{--}675\text{ cm}^{-1}$ corresponding to different types of =CH bonds [19, 20] was found.

In the spectra of sulfurized esters (Figure 1) the intensity of latter bands corresponding to double bonds is diminished. Instead, the bands in the range of $710\text{--}570\text{ cm}^{-1}$ and $550\text{--}450\text{ cm}^{-1}$, typical for stretching vibrations of C–S and S–S bonds appear. This confirms the addition of sulfur mainly at double bonds, according to the proposed scheme. The intensity of these bands is amplified when the number of bound sulfur increases. Due to the introduction of electronegative sulfur atoms to fatty acid esters molecules the intensity of the deformation vibrations of the C–H bonds in the hydrocarbon chains is grown with small offset of frequencies to negative values. Absorption band at 720 cm^{-1} corresponding to pender vibrations of methylene groups diminishes with sulfur content increasing. This indicates both an increasing in the number and length of sulfide

groups and the cross-linking of the hydrocarbon chains. The latter is well correlated with the changes in viscosity (Table).

In the spectra of Eterol-S₅ and Eterol-S₁₀ samples the bands at 967 cm^{-1} , corresponded to disubstituted ones are observed and starting with Eterol-S₂₀ the bands at $840\text{--}800\text{ cm}^{-1}$ corresponded to trisubstituted alkenes derivatives are occurred [19]. Such transformations in the structure are correlated to the change of Eterols-S_n viscosity with increasing of sulfur content in the entire temperature range (Figure 2).

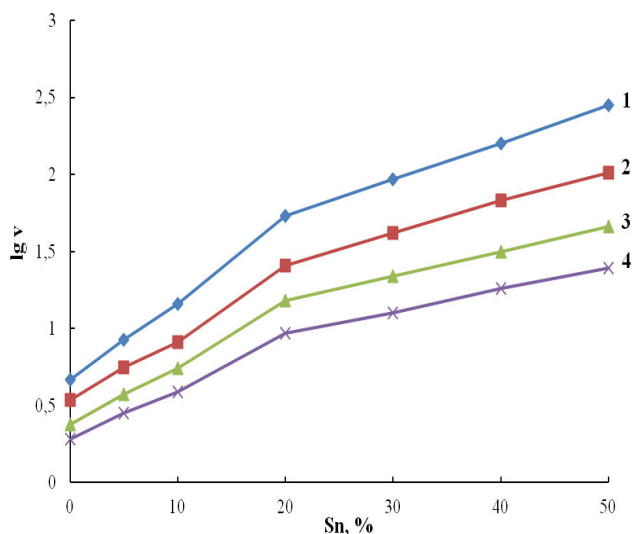
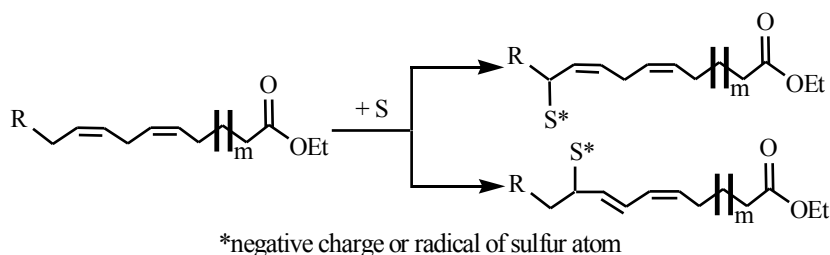
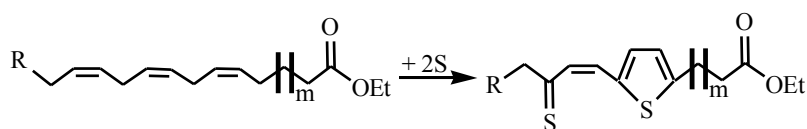


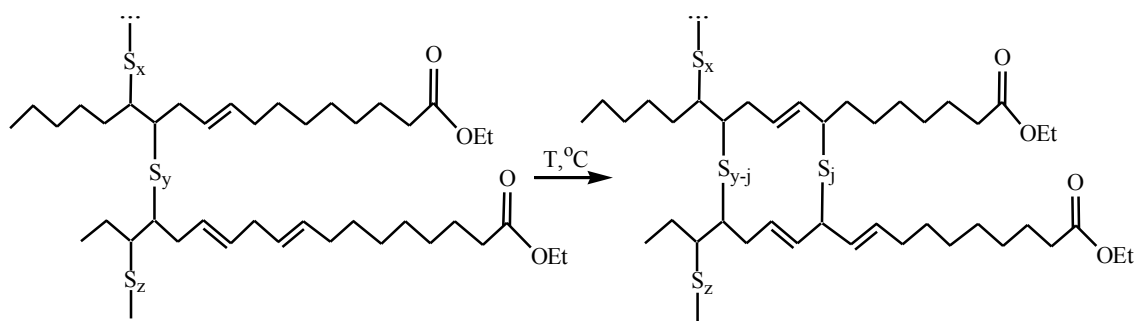
Figure 2. Semilogarithmic dependence of viscosity ($\lg v$) on the concentration of bound sulfur (S_n) at the temperature of, °C: 1 – 40, 2 – 60, 3 – 80, 4 – 100



Scheme 2.



Scheme 3.



Scheme 4.

On the other hand, it indicates that except sulfur addition to double bonds, a side reaction as the substitution of hydrogen by the α -methylene groups at these bonds occurs. This course may occur with preservation or migration of the double bonds follow by the temperature rising, according to the scheme 2 [15].

The results of iodine values analysis (Table) confirm this course of reaction.

Isomerization of the double bonds with formation of conjugate systems is accompanied by the darkening of the reaction products. The color is changed to purple or even black with temperature rising, that indicates both the increasing concentration of conjugated compounds and formation of the chromophore sulfur derivatives such as thioketones and thiophenes [1], according to the scheme 3.

The study of IR-spectra of Eterol-S_n samples found that the intensity of the bands in the region 710–570 cm⁻¹ (C–S bonds) and 550–450 cm⁻¹ (S–S bonds) increases with increasing the reaction duration due to the growing of sulfide chains and cross-linking of molecules. This statement is correlated with symbatic increasing of products viscosity and reaction time.

On the contrary, high temperature of sulfurization results in breaking of sulfide chains that is reflected in the IR-spectra (Figure 3) by decreasing intensity of stretching vibrations S–S. Thus, the intensity of the band at 800 cm⁻¹, corresponding to trisubstituted alkenes derivatives, is in-

creased and the band at 967 cm⁻¹, indicating the presence of two substituents at the double bonds, is reduced [19]. This is achieved by regrouping of polysulfide chains in more shorter and their subsequent distribution along the length of the hydrocarbon chain, due to the scheme 4.

In addition, we recorded that starting from 165 °C the evolution of hydrogen sulfide begins, which is enhanced with a further temperature growth. This course of the process is accompanied by reducing of yields and products viscosity, therefore, the optimal process temperature was taken 160–165 °C.

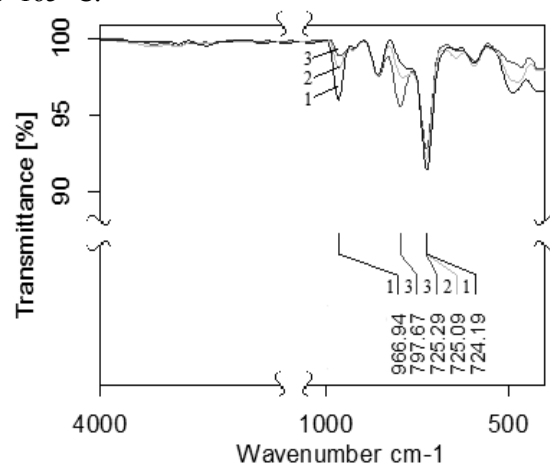


Figure 3. IR-spectrum of Eterol-S₁₅ samples occurred at various temperatures, °C: 1 – 160–165; 2 – 170–175; 3 – 205–215

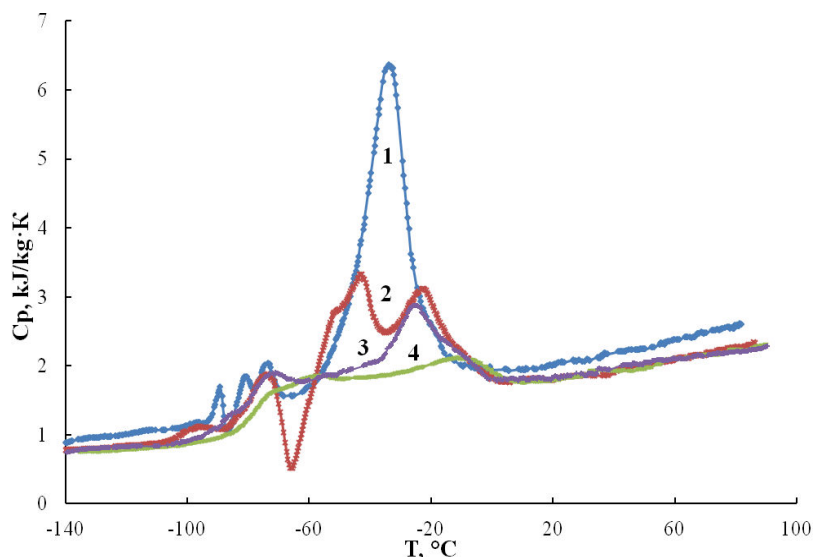


Figure 4. DSC-curves for FAEE (1) and Eterol-S₅-2, Eterol-S₁₀-3, Eterol-S₂₀-4

The study of phase transitions of sulfurized esters was performed by DSC, in the temperature range from minus 90 to 136 °C at the heating rate of 2 K/min and the same thermal history. The resulting temperature dependence of the specific heat on temperature for a series of samples Eterol-S_n is shown in Figure 4.

As you can see, three monotropic solid-phase transitions at temperatures (–89), (–81) and (–74) °C are observed on the DSC-curve for FAEE (curve 1) that is in good agreement with literature data [21]: saturated fatty acids with pair number of carbon atoms can form three polymorphic modifications as two metastable and one stable, and unsaturated ones, including oleic acid, are characterized by monotropic structural transitions. Such transitions in molecules of esters explain the formation of conformationally-disordered crystal structure [22]. Endothermic peak at a temperature of minus 34 °C corresponds to the melting of quasistable ethyl esters crystals.

For Eterol-S₅ sample (curve 2) the solid-phase transitions between crystalline modifications in the range of temperatures (–105 ...– 65) °C are occurred, but their exact identification is impossible due to the complex composition of the product. Instead of one clear endothermic melting peak a doublet with maximum at (–44) °C and (–23) °C occurs. The emergence of the peak plurality is caused by the reorganization or recrystallization as well as the presence of the crystals of different structure in the mixture [22].

With increasing of sulfur concentration in the product up to 10% (curve 3) the solid-phase transitions of crystalline modifications are not detected practically, that indicates a significant decreasing of unbound long hydrocarbon chains. However, free molecules capable to conformational ordering are remained, due to the presence of illegible endothermic melting peak at (–25) °C. According to this fact the amorphous and crystalline areas in system still exist in the system.

Begin with Eterol-S₂₀ the structure corresponds to oligomeric state already, as indicated by the absence of melting endotherm and disappearance of solid phase transformations between crystalline modifications. Glass transition temperature is increased with rising of sulfur content, confirming the growth of cross-linking degree of esters molecules [23].

Eterols-S_n are well dissolved and mixed with all known mineral oils and lubricating compositions for different purposes and functional additives to them. This is allowed to prepare the lubricants of various types and purposes as motor, gear, industrial oils, metalworking fluids, greases and others. The compositions with the most common industrial I-20A and naphthenic 5360 oils with sulfurized esters give the lubricants with significantly improved tribological characteristics.

Conclusions

1. The environmentally friendly method of obtaining of sulfur-containing additives for lubricants by sulfurization of fatty acid ethyl esters with elemental sulfur was developed.

2. The technical and economic parameters of sulfurization, were improved particularly, the process duration was reduced for 70–110 min compared to methyl esters and for 80–150 min to rapeseed oil with decreasing the temperature for 15–20 and 20–40 °C, respectively.

3. The structure and structural changes of the obtained products by IR-spectrometry and DSC, depending on the ratio of initial reagents, temperature and duration of the sulfurization process, sulfur content were determined

4. It was established, that Eterols-S_n form the composite materials for various purposes with improved tribological properties in the content of base oils.

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Синтез и структура серусодержащих противозадирных добавок к смазывающим материалам

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Разработан энергосберегающий, экологически безопасный способ получения противозадирных добавок к смазывающим материалам, который отличается среди известных улучшенными технико-экономическими параметрами сульфидирования ненасыщенных жирных эфиров масел элементной серой. Методами ИК-спектроскопии и дифференциальной сканирующей калориметрии установлено строение и структурные особенности полученных продуктов.

Синтез і будова сульфурвмісних протизадирних додатків до мастильних матеріалів

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Розроблено ресурсоенергозощадливий, екобезпечний спосіб одержання протизадирних додатків до мастильних матеріалів, який вирізняється з поміж відомих покращеними техніко-екномічними параметрами сульфидування ненасичених жирних естерів олій елементним сульфуром. Методами ІЧ-спектроскопії та диференціальної скануючої калориметрії встановлено будову і структурні особливості одержаних продуктів.