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# SYNTHESIS AND RESEARCH OF SULFUR, NITROGEN ORGANIC COMPOUNDS OBTAINED BASED ON ECOLOGICALLY PURE GLYCEROL DERIVATIVES

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**Abstract.** With the interaction of glycerol esters with sodium diethyldithiocarbamate derivatives of diethyldithiocarbamic acid were synthesized, containing active groups that turned out to be effective anti-seize and anti-wear additives to lubricating oils, not causing environmental pollution of the earth.

***Keywords:*** *glycerin, monochloroacetic acid, diethyldithiocarbamate, caprylic, additives, ecology, enanthic acid.*

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## 1. Introduction

The production of biodiesel from renewable energy sources of plants, algae in recent years has made glycerin a cheap chemical raw material for producing various products and semi-products used in the national economy (Casas *et al.*, 2010).

The consumption of glycerol in the world reaches more than 75% of the total. Unripe grapes and waste from the wine industry are good raw materials for the production of natural glycerin (Quispe *et al.*, 2013).

Glycerol derivatives are well absorbed by microorganisms. Most glycerol derivatives are easily destroyed by microorganisms, turning into non-toxic or low-toxic products, which plays an important role in solving environmental problems in its protection (Lyadov & Khadzhiev, 2017; http://eniw.ntm 17.11.2013; Al-Hasani *et.al.*, 2017).

Organic compounds containing active elements like sulfur-, nitrogen-, oxygen-, phosphorus-, chlorine are widely used in the national economy as drugs, herbicides, fungicides, lubricant additives, etc.

Among the additives that improve the lubricating properties of oils, sulfur-containing compounds occupy a special place, the high properties of which are due to the chemical interaction of their decomposition products at high friction temperatures with the metal surface, resulting in the formation of metal sulfides and disulfides, which have lower shear resistance and a lower melting point, than pure metals themselves, as a result of which seizure and seizure of metal surfaces are prevented (Kuliyev, 1985; Vinogradova, 1972).

These connections are used in gearboxes, rear axles of cars, tractors and other equipment. When vehicles move, exhaust gases, harmful substances that cause

environmental pollution of the earth and air are released, therefore the more efficiently the additives used are, the less harm is done to the environment.

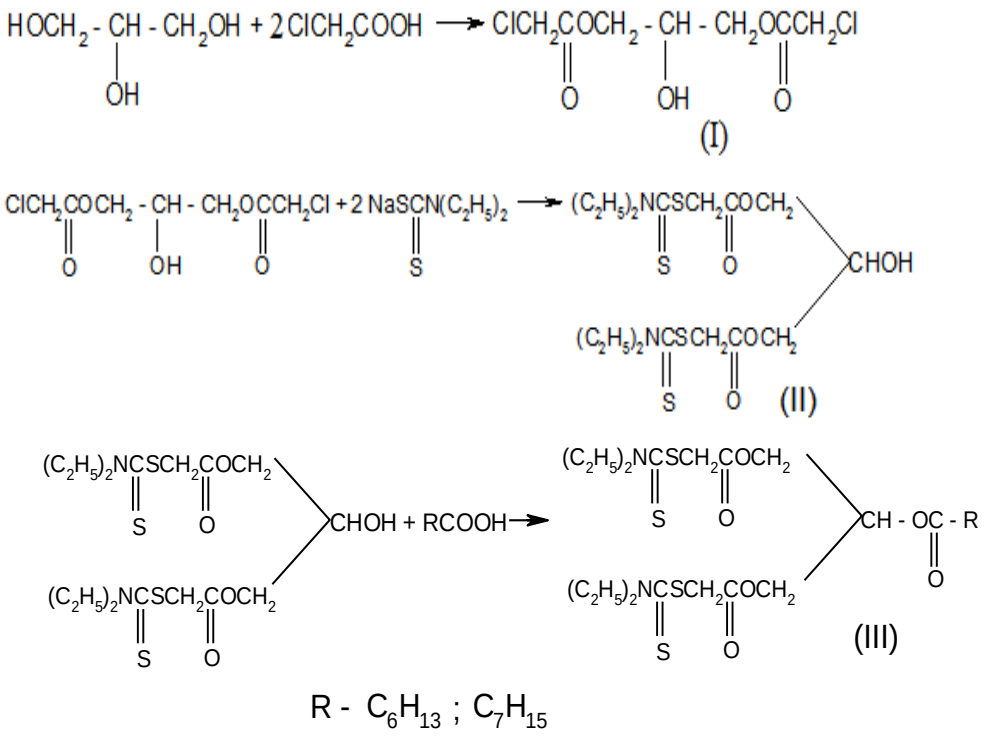
Among the sulfur-containing compounds, dithiocarbamates and their derivatives are effective extreme pressure additives and antioxidants. They are usually used in greases and in transmission oil compositions (Production, Application, Properties, 2012; Safarova *et al.*, 2013; Mustafaev *et al.*, 2013; Akchurina *et al.*, 2006). High operational properties of dithiocarbamate derivatives allow their use as lubricant compositions with high tribological properties (Charshv *et al.*, 2017).

Considering the possibility of enhancing the lubricating properties of compounds in the presence of active elements and polar groups in their composition, the synthesis of sulfur-organic compounds containing nitrogen, hydroxyl, ester and carbonyl groups enhancing the surface-active and lubricating properties of additives was of undoubted interest. Lubricating properties include anti-seize and anti-wear properties.

We have synthesized and investigated sulfur-nitrogen-organic compounds - derivatives of diethyldithiocarbamic acid, containing the above groups based on environmentally friendly esters of glycerol.

## 2. Material and Methods

Derivatives of diethyl dithiocarbamic acid were synthesized according to the scheme:




The syntheses were carried out as follows:

**Synthesis of 1,3-di (chloroacetyl) diglyceride (I).**

46 g (0.5 mol) of glycerol, 94.5 g (1 mol) of monochloroacetic acid, 5 g of toluene sulfonic acid (catalyst), 170 ml of toluene are taken in a Dean-Stark water separator

flask and the contents of the flask at a temperature of 110 °C are stirred for 8–10 hours until complete separation of the water. Water should stand out 18 ml. Upon completion of the reaction, the reaction product is washed with an aqueous solution of sodium bicarbanate, then with water, filtered off, the solvent is distilled off and distilled in high vacuum. The result is a light-yellow product, soluble in organic solvents, insoluble in water.

$C_7H_{10}O_5Cl_2$: B.P. 190-191/1,2 mm. hg.st;

$n_D^{20}$– 1,4843; $d_4^{20}$ – 1,4464; $MR_D$ – 48,49 (found.); $MR_D$ – 49,09 (calc.)

**Synthesis of 1,3-bis(diethylthiocarbamoylthio-acetyl)diglyceride (II).**

90 ml of acetone, 80 g (0.4 mol) of sodium diethyldithiocarbamate [$(C_2H_5)_2NC(S)$ SNa • $3H_2O$] are fed into a three-neck flask to 49g (0.2 mol) 1,3-di (chloroacetyl) diglyceride. The reaction is exothermic, as the diethyldithiocarbamate is supplied, the temperature in the flask rises to 40-45$^0$C. After 1 hour of stirring, the contents of the flask are heated to 50-55$^0$C and stirred for 5 hours. The reaction product is extracted with benzene, washed with water, the solvent is distilled off and distilled in vacuum to remove unreacted compounds. With the release of 62 g (89%), 1,3-bis(diethylthiocarbamoylthioacetyl)diglyceride was obtained a yellow liquid, soluble in organic solvents of lubricating oils and insoluble in water. Physico-chemical characteristics and its elemental analysis are given in Table 1.

The structure of the synthesized diglyceride was confirmed by IR spectroscopy. In the IR spectrum there are bands of stretching vibrations of the hydroxyl group in the region of 3478 cm$^{-1}$, and of carbonyl groups in the region of 1739 cm$^{-1}$. Both bands confirm the formation of diglyceride.

**Synthesis of 1,3-bis(diethylthiocarbamoylthioacetyl)diglyceride esters (III).**

In a flask with a Dean-Stark water separator, 47 g (0.1 mol) of 1,3-bis(diethylthiocarbamoylthioacetyl)diglyceride, 13 g (0.1 mol) of enanthic acid, 0.5 g of toluenesulfonic acid as a catalyst, 80 ml of toluene added and at a temperature of 110°C is stirred until complete separation of water. Water should stand out 1.8 ml. The reaction product is washed with water, with an aqueous solution of sodium bicarbonate, then with water, filtered, the solvent is distilled off and distilled in vacuum. As a result, 1,3-bis (di-ethylthiocarbamoylthioacetyl) diglyceride enanthate was obtained.

Similarly, 1,3-bis (diethylthiocarbamoylthioacetyl) diglyceride caprylic ester was obtained.

The physical-chemical characterization and elemental analysis of the enanthic and caprylic esters are listed in Table 1.

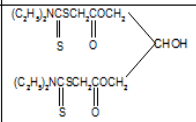
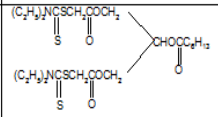
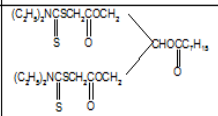
I-III compounds were purified using liquid column chromatography (Mammadov *et al.,* 2019). Liquid column separation was carried out on an adsorption column with 1.5 m in length and consisting of three sections: with diameters 4 sm, 3 sm, 1.5 sm. ACK silica gel (GOST 3956-54) was used as the adsorbent. Column separation was monitored by thin-layer chromatography and determination of refractive indices. Hexane, benzene and isopropyl alcohol were used as eluents.

The structure of the enanthic and caprylic triglyceride esters was confirmed by IR spectroscopy. In the IR spectra of these compounds, the absorption band of the valence vibrations of the hydroxyl group is absent. The absorption band of the vibrations of the carbonyl group is present in the region of 1743 cm$^{-1}$ and 1728 cm$^{-1}$. It is the absence of

vibrations of the hydroxyl group that proves the formation of enanthic and caprylic esters.

Diethyldithiocarbamic acid derivatives were studied as extreme pressure and anti-wear additives for lubricating oils.

**Table 1.** Physical-chemical characterization and elemental analysis of the enanthic and caprylic esters

| № | Compounds | Exit, % | $n_D^{20}$ | $d_4^{20}$ | $MR_D$ | | Elemental analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Found | Calc. | Found | | | | Calculated | | | |
| | | | | | | | C | H | S | N | C | H | S | N |
| I |  | 89 | 1.5860 | 1.2443 | 126.76 | 126.58 | 43.12 | 6.08 | 27.61 | 5.66 | 43.40 | 6.38 | 27.23 | 5.95 |
| II |  | 90 | 1.5550 | 1.1698 | 159.70 | 159.90 | 49.69 | 7.15 | 21.43 | 4.63 | 49.48 | 7.21 | 21.99 | 4.81 |
| III |  | 90 | 1.5471 | 1.1541 | 163.65 | 163.78 | 50.17 | 7.05 | 21.18 | 4.22 | 50.33 | 7.38 | 21.47 | 4.69 |

## 3. Data and Methods

The aim of the work was to study synthesized sulfur-nitrogen-containing organic compounds - derivatives of dithiocarbamic acid as anti-seize and anti-wear additives, using chemical raw materials that do not cause ecological land problems and negative interaction on the air and the environment.

In this sense, glycerol derivatives turned out to be very good chemical raw materials. The anti-seize properties were determined by the ASTM D2596 test method, the estimated indicators were the badiss index, the critical load, the welding load. According to ASTM test method D2266 anti-wear properties were determined; estimated indicators – the diameter of the wear (mm).

## 4. Application and Results

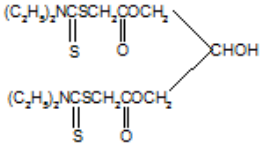
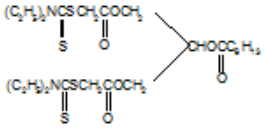
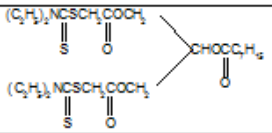
The extreme pressure and anti-wear properties of dithiocarbamic acid derivatives were determined at a concentration of 10,6 mmol in MS-20 oil. The test results are shown in Table 2.

As can be seen from the test results listed in the table, dithiocarbamic acid derivatives improve the extreme pressure and anti-wear properties of the oil. 1,3-bis(di-ethylthiocarbamoylthioacetyl) diglyceride enanthic and caprylic esters turned out to be more effective in anti-wear properties, improving the teaser index to 0.60 mm.

The combination of the ester group with two functional dithiocarbamine residues  due to synergism makes them effective.

Thus, dithiocarbamic acid derivatives proved to be quite effective anti-seize and anti-wear additives to lubricating oils and, due to their effectiveness, do not cause ecological pollution of the earth and the environment.

**Table 2.** Indicators of antiwear and extreme pressure properties of test compounds

| № | Compounds | Concentration in oil, mmol | Anti-seize properties acc. to ASTM D 2596 | | | Anti-wear properties acc. to ASTM D2266 |
|---|---|---|---|---|---|---|
| | | | Badass index, N | Critical load, N | welding load, N | Wear diameter, mm |
| 1. | MC-20 oil | – | 330 | 784 | 1560 | 0.75 |
| 2. |  | 10.6 | 558 | 1260 | 3479 | 0.67 |
| 3. |  | 10.6 | 550 | 1260 | 3479 | 0.60 |
| 4. |  | 10.6 | 536 | 1120 | 3479 | 0.62 |

## 5. Conlusions and Recommendations

Synthesized derivatives of dithiocarbamic acid with respect to their effective anti-seize and anti-wear properties are recommended for creating transmission oil TM-4.

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