

UDC 547.729

**SYNTHESIS OF SOME ETHERS OF DIETHYLDITHIOCARBAMIC ACID AND INVESTIGATION OF THEIR INFLUENCE ON ANTI-WEAR AND EXTREME PRESSURE PROPERTIES OF LUBRICATING OILS****A.Kh. Kerimov, Kh.A. Mamedova, E.S. Dzhafarova, I.A. Khudiyeva**

*Institute of Poly mer Materials of the National Academy of Sciences of Azerbaijan,  
S.Vurgun str., 124, Sumgait Az 5004, Azerbaijan Republic  
E-mail: [kerimov.alverdi@mail.ru](mailto:kerimov.alverdi@mail.ru)*

*Received 20.05.2022*

*Accepted 09.07.2022*

**Abstract:** *By the reaction of sodium diethyldithiocarbamate trihydrate with chlorosubstituted addends – allyl-, tetrahydrofurfuryl monochloroacetate, allyl-3-chloropropanoate and 4-chloromethyl-1,3-dioxolane, the appropriate ethers of diethyldithiocarbamic acid were synthesized. The influence of their composition and structure on the quality of lubricants was investigated.*

**Keywords:** *ethers of diethyldithiocarbamic acid, anti-wear properties, lubricity, critical load.*

**DOI:** 10.32737/2221-8688-2022-3-223-228

**Introduction**

The derivatives of dialkyl(aryl) dithiocarbamic acids are one of the most widespread reagents in practice, combining heteroatoms of various nature (N, O, S) in the molecule which largely stipulates the expansion of their application (in chemistry, metallurgy, medicine, agriculture, etc.), on the one hand, and stimulates the ever-increasing interest of researchers of various scientific profiles, on the other hand. However, in sufficiently extensive assortment of the derivatives of dithiocarbamic acid, owing to some circumstances (possibly the accessibility of raw materials), the ethers of diethyldithiocarboxylic acid (DEDTCA) are dominant [1]. They are used as multifunctional additives to lubricating oils [2], iniferters of the radical polymerization of olefins, allowing to control the polydispersity of the obtained matrix [3], accelerators of vulcanization of rubbers and antioxidants in the rubber industry [4], biologically active substances [5] and play an important role as intermediate synthons in organic synthesis [1. p. 9-13].

It should be noted that one of the actual directions of application of DEDTCA ethers is the creation of lubricating compositions with improved or high exploitation properties on their basis. As is known, at low qualities of

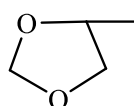
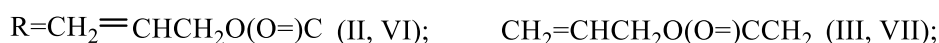
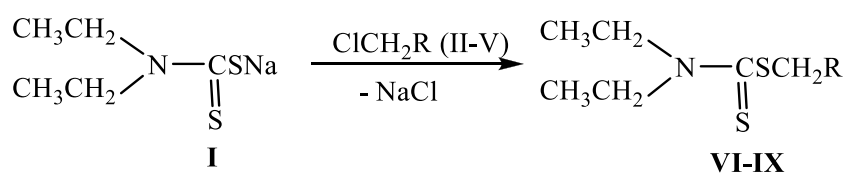
lubricating oils, the friction between the metal surfaces of machine details and aggregates grows sharply and the latter ones come into direct contact, which leads to appearance of roughness on their surface and ultimately to abrasion and wear. Consequently, the rapidly growing level of technical progress in machine building requires an increase of the exploitation properties of lubricants used to decline the abrasion and wear of the surfaces of metallic details, and it is almost impossible to prevent these phenomena without the use of additives to lubricating oils. Thus, the search for additives increasing the efficiency of lubricating compositions attracts the close attention of researchers [6]. DEDTCA ethers, combining

dithiocarbamate fragment  $\left[ \begin{array}{c} \diagup \\ \text{N}-\text{C}(=\text{S})\text{S} \cdot \\ \diagdown \end{array} \right]$  with an ester group and functionally substituted radicals in the molecule play an important role in solution of this problem, which apparently favor the formation of strong films on the contacting surfaces of metallic details of machines and aggregates and, consequently, improve not only the anti-wear efficiency of lubricating compositions, but also provide their lubricating activity [7]. This notwithstanding, the investigation of the synthesis reactions of

DEDTCA ethers and the possibility of creation of the lubricating compositions with high exploitation properties on their basis are a comparatively little-studied area of organic synthesis, and the available reports are of episodic character and besides, they have a preparative value [8].

In this paper the results of investigation of the synthesis reaction of functionally substituted DEDTCA ethers (VI-IX) by alkylation of

sodium diethyldithiocarbamate (DEDTCNa) with the corresponding chlorine-containing addend (II-V) and study of their influence on the anti-wear and extreme pressure properties of lubricating compositions are presented. The synthesis of compounds (VI-IX) was carried out according to a well-known methodology well-known [5. pp. 1-9], in an aqueous medium on the scheme as follows:



(IV, VIII);



CH<sub>2</sub>O(O)=C (V, IX).

The compound (I) used as an initial material, is a publicly available reagent produced by the chemical industry [9]. The compound (II) is a commercial product [10], and ethers (III, IV) were obtained by esterification of monochloroacetic and 3-chloropropionic acid with allyl and tetrahydrofurfuryl alcohol (respectively) according to a known methodology [11]. The compound (V) was synthesized by the formaldehyde reaction with 3-chloro-1,2-epoxypropane according to the methodology [12].

The synthesized dithiocarbamates [S-(carballyloxy)methyl- (VI), S-(carballyloxy)ethyl-(VII), S-(1,3-dioxo-4-cyclohexyl)methyl- (VIII) and S-(carbtetrahydrofurfuryloxy)methyl-N,N-diethyldithiocarbamate (IX)] are transparent liquids without odor. They are insoluble in water, but well soluble in organic compounds

(ether, CCl<sub>4</sub>, CHCl<sub>3</sub> etc) and lubricating oils.

It should be noted that the details of the synthesis, composition and structure, as well as dithiocarbamate constants (VI-IX) are given in work [5] dealing with the investigation of their biological activity. Only a description of the reaction equation (in a slightly different form) of the synthesis of compounds (VI-IX) and Table (Table. 1), reflecting their physical-chemical constants was included in this work.

Based on the fact that the compounds (VI-IX) synthesized by us possess potential biological activity [5], they are well dissolved in lubricating oils, have a high boiling point and thermal stability, i.e. meet the basic requirements for chemical compositions used as additives to lubricating oils [13] and with the aim of creation of a lubricant with improved or high exploitation properties, their influence on the anti-wear and extreme pressure properties of the base oil AK-15 was analyzed.

### Experimental part

The efficiency of dithiocarbamates (VI-IX) was determined by their testing in a mixture with lubricating oil AK-15. The tests were

carried out jointly with the collaborators of the laboratories

**Table 1.** Yields, constants and data of elemental compositions of the compounds (VI-IX).

№ of compound	Yield, %	B.p. °C (P, mm, merc.c.)	d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>20</sup>	MR <sub>D</sub>		Found, %				Calculated, %				
					Found	Calculated	C	H	N	S	C	H	N	S	
VI	89.7	160-162/0.5	1.1375	1.5590	70.2200	70.1100	48.52	6.88	5.62	25.88	C <sub>10</sub> H <sub>17</sub> NO <sub>2</sub> S <sub>2</sub>	48.56	6.92	5.66	25.92
VII	88.5	192-194/0.5	1.1213	1.5510	74.3679	74.7700	50.48	7.29	5.33	24.50	C <sub>11</sub> H <sub>19</sub> NO <sub>2</sub> S <sub>2</sub>	50.54	7.33	5.36	24.53
VIII	74.5	178-180/1	1.1623	1.5690	66.30	65.76	45.89	7.31	5.93	27.22	C <sub>9</sub> H <sub>17</sub> NO <sub>2</sub> S <sub>2</sub>	45.92	7.29	5.96	27.24
IX	90.3	228-230/0.5	1.1614	1.5550	80.5496	79.7000	49.42	7.23	4.78	21.97	C <sub>12</sub> H <sub>21</sub> N S <sub>2</sub> O <sub>3</sub>	49.46	7.26	4.80	22.00

**Table 2.** Data characterizing the thermal stability and anti-wear and extreme pressure properties of AK-15 oil containing 3% of the corresponding ester of diethylthiocarbamic acid (VI-IX).

№ of comp.*	Initial decomposition temperature, °C	Samples of the lubricating composition	Additive concentration in oil, %	Tribological properties of the lubricating composition			
				Tease index. I <sub>t</sub>	Critical loading. P <sub>c</sub>	Welding load, P <sub>w</sub>	Diameter of wear spot. D <sub>w</sub>
VI	175	VI+AK-15	3	485	980	3097	0.76
VII	185	VII+ AK-15	3	500	980	3097	0.75
VIII	200	VIII+ AK-15	3	513	1098	2764	0.85
IX	200	IX+ AK-15	3	553	1098	3479	0.76
Oil AK-15			—	323	617	980	0.78

\* Compounds are arranged on increase "Tease Index"

"Synthesis of additives and theoretical bases of mechanism of their action" and "Additive and composition of additives to transmission and industrial oils" of the Institute of "Chemistry of Additives" named after Acad. A.M. Guliyev of the National Academy of Sciences of Azerbaijan. The tests were carried out on four-ball friction machine TR-4, on steel balls of mark ShKh-15, with a diameter of 12.7 mm in air at room temperature and a sliding rate of 1400 rev.min The tested compounds (VI-IX) were injected into AK-15 oil in keeping with international standards (ASTM D 2596 and ASMD 2266).

The obtained quantitative data in comparison with the corresponding indices of the base oil AK-15 are shown in Table 2. The efficiency of the compounds tested as anti-wear and extreme pressure additives was investigated as 3% composition of the appropriate compound in the base oil AK-15. The anti-wear and

extreme pressure characteristics of the obtained compositions were determined on the method of stepwise sinkage of balls. For each load, the friction was carried out on balls with fresh surface in the presence of a new portion of the composition. After each experiment, the diameters of the wear spots on the lower balls were measured in two mutually perpendicular directions. The diameter average values of the wear spots ( $d_{av}$ ) from six measurements were taken as the final result. During the testing process of each compound, the appropriate jamming loads were fixed and the tease index was calculated.

The indices characterizing the thermal stability of dithiocarbamates determined on a derivatograph of OD-102 T type of the Paulik system (Hungary) on the method [14] and the results of their testing as additives to the base oil AK-15 are given in Table 2.

### Results and discussion

As follows from Table, the thermal stability of the tested dithiocarbamates (VI-IX) (which have the same acid residue –  $(Et_2N-C(=S)S^*)$ ), is essentially dependent on the composition and nature of the substituted S-alkyl radical, and, as expected, the dithiocarbamates (VI, VII) containing carboxyallyl fragment in the  $\alpha$  – or  $\beta$  – position to the acid residue, possess (in comparison with compounds VIII, IX) somewhat less stability against temperature influences. The noted phenomenon is, apparently, a consequence of the possible conjugation of  $\pi$ -electron system of the double bond of the allyl group with the same system of the carbonyl oxygen atom, owing to which the heterolytic break of S-CH<sub>2</sub> bond is somewhat activated. This assumption is indirectly confirmed by the considerably high temperature of the beginning of decomposition of compounds (VIII, IX), which was stipulated by the absence of substituent unsaturated bond in their alkyl fragment.

It was established that the efficiency of the compounds tested as anti-wear and extreme pressure additives to the base oil AK-15, which can favor an increase of the service life of friction units of metal surfaces of machines and

mechanisms, essentially depends not only on the composition and structure, but also on their stability in action of higher temperatures. Thus, an increase of the relative thermal stability of esters (VI-IX) is accompanied by an increase of the characteristic indices ( $I_t$ ,  $L_c$ ,  $L_w$ ) of the lubricating composition in comparison with the corresponding indices of oil AK-15 (Table 2). Moreover, these indices have a minimum value (except for the welding load) in a case of the compounds (VI, VII) and a maximum value in a case of the compounds (VIII, IX), i.e. the thermal stability of the tested compounds has a good correlation with their anti-wear and extreme pressure efficiency.

The availability of potentially electron-donors atoms of thionic and thiol sulfur in the molecules of the tested esters essentially increases their activity to metals, which leads to modification of rubbing surfaces and the realization of high efficiency of the composition used as anti-wear and extreme pressure lubricants [14.p.50]. The role of the carboxyl group consists not only of increase of the extreme pressure properties of the compositions [8. p. 3/13], but in improving their lubricity as well.

### Conclusions

Thus, the above-listed quantitative data (Table. 2) indicate that the tested compounds (VI-IX) allow increasing the tribological properties of the base oil AK-15 in the complex, and can be recommended as effective additives for use in various industries.

*The author expresses his deep gratitude to I. P. Ismailov for the help provided during the execution of the corresponding experiments and the design of this work.*

### References

1. Byrko V. M. Dithiokarbamaty. Moscow: Nauka Publ., 1984, 342 p.
2. Mustafaev N.P., Gadzhieva I. B., Alieva A.B., Novotorzhina N.N. Synthesis of amino-containing derivatives of thiocarbon acids and their investigation as polyfunctional additives. *Azerb.Chem.J.*, 2007, no. 3, pp. 147-151.
3. Nikolaev A.F., Krizhanovsky V.K. Technology of polymer materials. Saint-Petersburg: Profession Publ., 2008, 533 p.
4. Blokh G.A. Organic accelerators of vulcanization of rubbers. L.: "Khimiya", 1972, 559 p.
5. Alverdi Karimov, Arzu Orujova, Pahram Taslimi, Nastoran Sadeqian, Bahtiyar Mammadov, Halide Sedef Karaman, Vaqif Farzaliyev, Afsun Sujayev, Reser Tas, Saleh Alwasel, Ilhami Gülçin. Novel functionally substituted esters based on sodium diethyldithiocarbamate derivatives: Synthesis, characterization, biological activity and molecular docking studies. *Bioorg. Chem.* 2020, vol. 99. 103762 DOI: [10.1016/j.bioorg.2020.103762](https://doi.org/10.1016/j.bioorg.2020.103762)
6. Kerimov A.H., Orudzheva A.T., Mamedova Kh.A. The dioxolanation reaction of cyclohex-3-ene-1-carbaldehydes with 1,2-diols and properties of the obtained products.// *CHEMICAL PROBLEMS*. 2019. № 1. p. 93-99.
7. Kuliyeu A.M. Chemistry and technology of additives to oils and fuels. L.: "Khimiya", 1985. 312 p c.
8. Akchurina T.H., Efendiyeva Kh.K., Aliyeva M.N., Hasanova A.M. Thermal stability and chemical activity in relation to metals of some acetoxy-, benzoyloxymethyl and acetoxy-, vinylcarboxyethyl ethers of xanthogenic, dithiophosphoric and dithiocarbamic acids. *Oil refining and petrochemistry*. 2012, no. 2, pp. 46-50.
9. A.s. USSR SU1006431 (1983). Kuliyeu A.M., Kuliyeu M.A., Kulibekova T.N., Mkhitaryan Sh.A. Acetoxymethyl ether of diethyldithiocarbamic acid as an extreme pressure additive to lubricating oils. B.I. 1983. № 11.
10. Mustafaev N.P., Kuliyeu M.A., Mustafaev K.N., Kulibekova T.N., Kakhramanova G.A., Safarova M.R., Novotorzhina N.N. Synthesis of acyloxyalkyl esters of thiocarbonic and dithiocarbamic acids. *Russian Journal of Organic Chemistry*. 2013, vol. 49, pp. 198-203. DOI: [10.1134/S1070428013020048](https://doi.org/10.1134/S1070428013020048)
11. Chemical reagents and high-purity chemical substances. Catalog. M.: "Khimiya". 1990, p. 14, № 011526, TU 6-09-08-1654-83.
12. Aliyeva E.S., Kerimov A.H., Babayev M.G. Synthesis and some conversions of halogen alkyl ethers of 3-cyclohexene-1-carboxylic acids. *Zhurnal organicheskoi khimii*. 1992, vol. 22, no. 4, pp. 706-711.
13. Kerimov A.H. Synthesis of 1,3-dioxolan derivatives based on carbocyclic aldehydes and study of their properties. *Zhurnal organicheskoi khimii*. 2001, vol.37, no.1, pp. 144-147.
14. Akchurina T.Kh. Thermal stability of ethers of dithiocarbamic acid. *Oil refining and petrochemistry*. 2013, no. 9, pp. 32-35

## DIETİLDİTİOKARBAMİN TURŞUSUNUN BƏZİ EFİRLƏRİNİN SİNTEZİ VƏ ONLARIN SÜRTGÜ YAĞLARININ YEYİLMƏ VƏ SİYRİLMƏ XASSƏLƏRİNƏ TƏSİRİNİN TƏDQIQI

Ə.X. Kərimov, X.A. Məmmədova, E.S. Cəfərova, I.Ə. Xudiyeva

*AMEA Polimer materialları institutu.  
Az 5004 Sumqayıt, S.Vurğun küç., 124:  
E-mail: [kerimov.alverdi@mail.ru](mailto:kerimov.alverdi@mail.ru)*

**Xülasə:** Natrium dietilditiokarbamatın trihidratının xloraddentlərlə -- allil-, tetrahidrofurfurilmonoxlorasetatla, allil-3-xlorpropanoatla və 4-xlorometil-1,3-dioksolanla reaksiyası əsasında, dietilditiokarbamin turşusunun müvafiq efirləri sintez edilmiş və onların tərkib və quruluşunun sürtgü yağlarının xassəsinə təsiri tədqiq edilmişdir.

**Açar sözlər:** dietilditiokarbamin turşusunun efirləri, yeyilməyə qarşı davamlılıq, islatma dərəcəsi, böhran yükü

## СИНТЕЗ НЕКОТОРЫХ ЭФИРОВ ДИЭТИЛДИТИОКАРБАМИНОВОЙ КИСЛОТЫ И ИССЛЕДОВАНИЕ ИХ ВЛИЯНИЯ НА ПРОТОВОИЗНОСНЫЕ И ПРОТИВОЗАДИРНЫЕ СВОЙСТВА СМАЗОЧНЫХ МАСЕЛ

А.Х. Керимов, Х.А. Мамедова, Э.С. Джафарова, И.А. Худиева

*Институт полимерных материалов Национальной АН Азербайджана  
AZ 5004 Сумгайыт, ул. С.Вургуна, 124.  
E-mail: [kerimov.alverdi@mail.ru](mailto:kerimov.alverdi@mail.ru)*

**Аннотация:** Реакцией тригидрата диэтилдитиокарбамата натрия с хлорзамещенными аддендами – аллил-, тетрагидрофурфурилмонохлорацетатом, аллил-3-хлорпропанатом и 4-хлорметил-1,3-диоксоланом синтезированы соответствующие эфиры диэтилдитиокарбаминаминовой кислоты. Исследовано влияние их свойств и структуры на качество смазочных материалов.

**Ключевые слова:** эфиры диэтилдитиокарбаминаминовой кислоты, противоизносные свойства, смазываемость, критическая нагрузка