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SYNTHESIS OF AMINOMETHYL DERIVATIVES OF 3-MERCAPTO-2-HYDROXYPROPYL-1-ISOBUTYL ETHER AND THEIR STUDY AS PROTECTIVE ADDITIVES TO LUBRICANT OILS

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Received 07.09.2022
Accepted 26.12.2022

Abstract: *The electrochemical corrosion prevention of engines and mechanisms is a task of great national, economic and defense importance. Lubricating oils commonly used in engineering do not have sufficient protective properties and are unable to effectively protect it from corrosion, both during operation and during short-term and long-term inactivity. One of the simplest and most rational ways to solve this problem is the use of lubricants containing effective protective (conservation) additives, which, without worsening the normal working properties of oils provide them conservation properties. By the action of 3-mercapto-2-hydroxypropyl-1-isobutyl ether, taken as a synthon, with secondary aliphatic and heterocyclic amines under the conditions of the Mannich reaction, a number of aminomethyl derivatives were synthesized. Aminomethyl derivatives of 3-mercapto-2-hydroxypropyl-1-isobutyl ether are dissolved well in oils and are stable during storage. The protective properties of the synthesized compounds were studied in M-12 oil. The best test results were obtained with 3-piperidinomethilthio-2-hydroxypropyl-1-isobutyl ether - at a concentration of 1% to the lubricating oil M-12, the corrosion of a steel plate in a humid chamber is 3%, in sea water after 24 hours – 5%, the corrosion of a steel plate under the action of a 0.1% acid solution HBr – 3,5%. These results are higher than those of the standard - industrial additive urea succinimide. (SIM).*
Keywords: *Potassium hydrosulfide, corrosion, protective additive, lubricant oils, piperidine, morpholine*
DOI: 10.32737/2221-8688-2023-1-48-56

Introduction

Various weather-climatic and atmospheric conditions during the operation of equipment require the adoption of appropriate measures to protect it both during operation and during storage, transportation and long-term storage.For these purposes, protective additives for lubricating oils are used, providing them with required working-conservation properties.

One of the most important problems in creating promising additives and their compositions is the study of the effect of their composition on various characteristics of the state of the surface layers of metals, including corrosion damage.

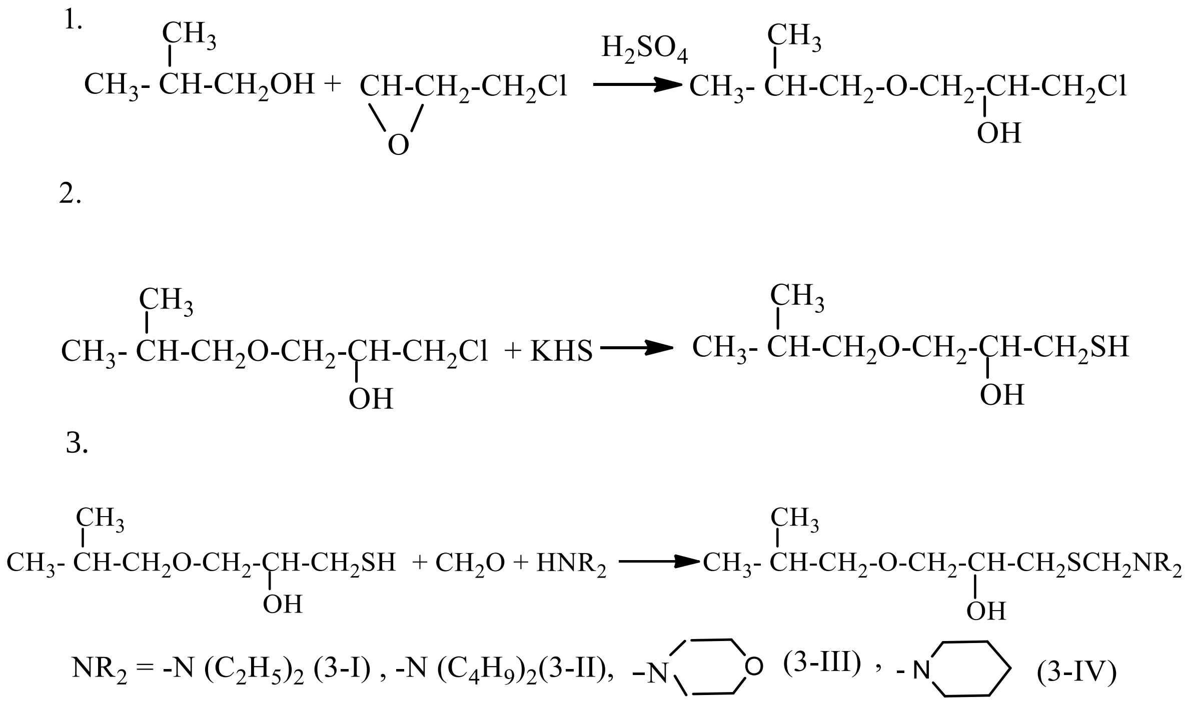
The contradictory requirements when using additives for operating-conservation oils under these conditions is that additives with high surface activity are desirable for realizing a high level of functional properties that provide a protective effect.. However, the high surface activity of the additives is associated with the possibility of their action in the direction of the adsorption decrease in the strength of the surface layers of the metal in contact with this additive.

Analysis of the literature [1-11] shows that compounds containing various functional groups and heteroatoms, such as N-, S- , are used as protective organic compounds. These compounds are surfactants that protect metals from electrochemical corrosion in the electrolyte-petroleum-metal system.

Results and their discussion

To obtain the above-mentioned compounds, 3-mercapto-2-hydroxypropyl-1-isobutyl ether was used as a synthon. Aminomethyl derivatives were synthesized by the interaction of formalin, secondary aliphatic and heterocyclic amines with 3-mercapto-2-hydroxypropyl-1-isobutyl ether by the Mannich reaction.

The reactions were carried out in line with to the following scheme:



Obtaining 3-chloro-2-hydroxypropyl-1-isobutyl ether (1)

30 g of ephichlorohydrin and 36 g of isobutyl alcohol were added to a 100 ml three-necked reaction flask. Then, 3 ml of 98% sulfuric acid was added dropwise to the mixture. Then, the mixture was stirred at a temperature of 90-95^0 C for 6 hours. After completion of the reaction, the mixture was extracted with toluene, washed with water, dried over Na_2SO_4, and the toluene was distilled off. The residue was distilled under vacuum in an oil bath. Physical-chemical characteristics of 3-chloro-2-hydroxypropyl-1-isobutyl ether are given in Table 1. The structure and composition of 3-chloro-2-hydroxypropyl-1-isobutyl ether were confirmed by ^{1}H, ^{13}C NMR spectroscopy and elemental analysis. Signals of the ^{1}H, ^{13}C NMR spectrum of 3-chloro-2-hydroxypropyl-1-isobutyl ether are as follows: ^{1}H NMR spectrum (fig.1), (C_6 D_6, δ, ppm): 0.78 (d.,6H,CH_3), 1.7 (m., 1H, <u>CH</u>-$(CH_3)_2$), 2.93 (d.,2H, CH_2Cl), 3.24 (m.,4H,CH_2O), 3.41 (m.,<u>CH</u>OH).

^{13}C NMR spectrum (fig.2), (C_6 D_6 , δ, ppm): 18.94 (CH_3), 28.18 ($CH(CH_3)_2$), 46.06 (CH_2 Cl), 72.89 (CH_2 O CH_2 -), 78.03 (CHOH).

Synthesis of 3-mercapto-2-hydroxypropyl-1-isobutyl ether (2)

12 g of 3-chloro-2-hydroxypropyl-1-isobutyl ether, 20 ml of ethyl alcohol and potassium hydrosulfide (KHS), which was obtained by the reaction KOH+ H_2S= KHS+H_2O (in a solution of 7 g of KOH within 0.5 hours served H_2S) were placed in a three-necked reaction flask with a capacity of 100 ml, equipped with a mechanical stirrer, a condenser and a thermometer.

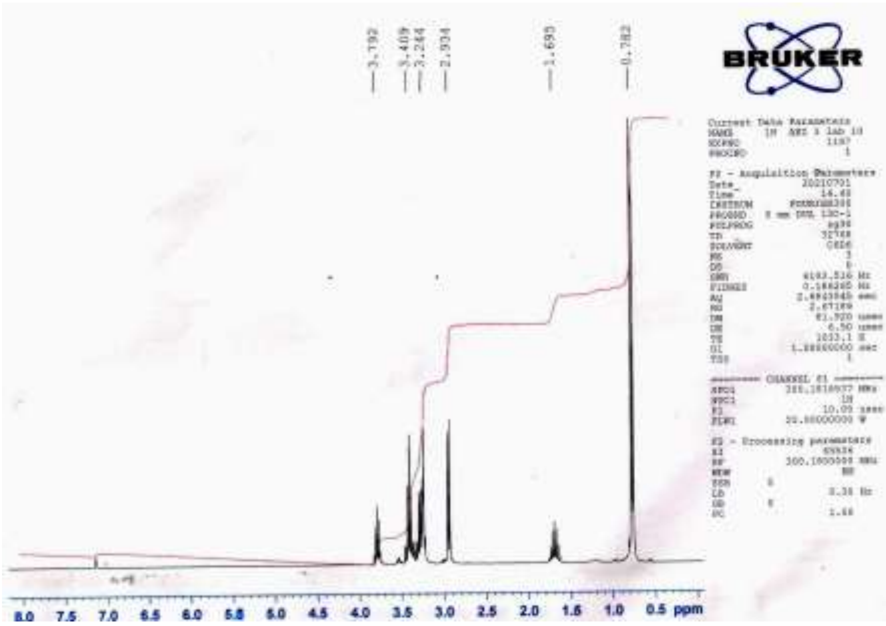


Fig.1. ^{1}H NMR spectrum of 3-chloro-2-hydroxypropyl-1-isobutyl ether

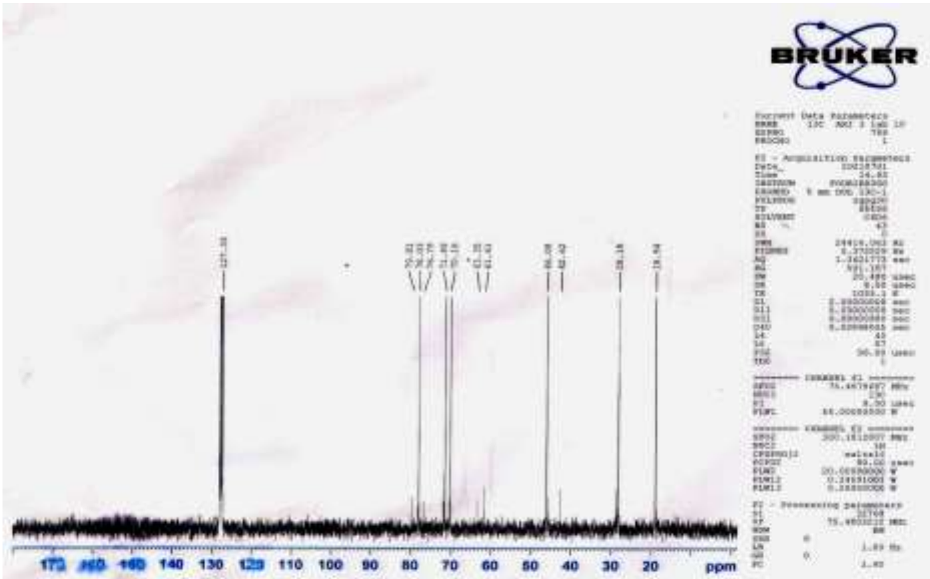


Fig. 2. ^{13}C NMR spectrum of 3-chloro-2-hydroxypropyl-1-isobutyl ether

The reaction mixture was stirred at a temperature of 75-80^{0} C for 5-6 hours. Then it was extracted with benzene, washed, dried over Na_2SO_4, the residue was distilled under vacuum on an oil bath. Physical-chemical constants of the obtained compounds are given in table 1. The structure and composition of 3-mercapto-2-hydroxypropyl-1-isobutyl ether was confirmed by ^{1}H, ^{13}C NMR spectroscopy and elemental analysis. The signals of the ^{1}H, ^{13}C NMR spectrum of 3-mercapto-2-hydroxypropyl-1-isobutyl ether are as follows: ^{1}H NMR spectrum (fig. 3), (C_6D_6, δ, ppm): 0.81 (d., 6H, CH_3), 1.75 (m., 1H, $(CH_3)_2\underline{CH}$), 2.70 (m., 1H, $\underline{CH}$OH), 3.02 (d., 4H, CH_2O), 3.37 (d., 2H, CH_2SH), 3.94 (s., 1H, SH), 4.34 (s., 1H, OH).

^{13} C NMR spectrum (fig. 4), (C_6D_6, δ, ppm): 19.13 and 28.27 (CH_3), 36.83 ($(CH_3)_2\underline{CH}$), 70.01($\underline{CH}$OH), 73.69(CH_2-O- CH_2), 78.05(CH_2-SH).

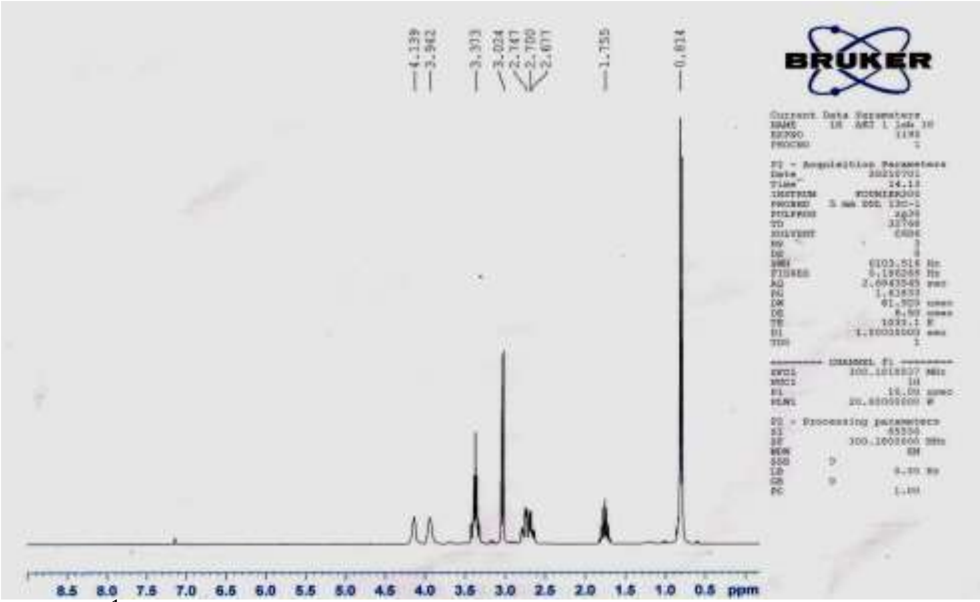


Fig. 3. ^{1}H NMR spectrum of 3-mercapto-2-hydroxypropyl-1-isobutyl ether

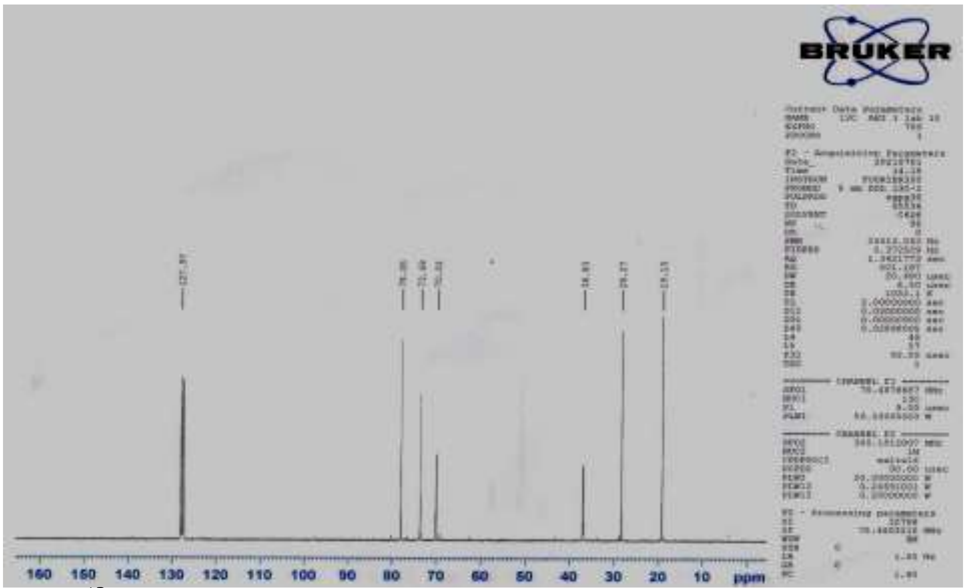


Fig. 4. ^{13}C NMR spectrum of 3-mercapto-2-hydroxypropyl-1-isobutyl ether

Syntesis of 3-piperidinomethylthio-2-hydroxypropyl-1-isobutyl ether (3-IV)

6 ml of a 37% aqueous solution of formalin and 20 ml of benzene were placed into a reaction flask with a capacity of 100 ml, and added dropwise 3.6 g of piperidine at a temperature of 20^0 to 25^0 C. The temperature of the mixture was raised to 30^0-35^0 C, and then 5.5 g of 3-mercapto-2-hydroxypropyl-1-isobutyl ether dissolved in 15 ml of benzene was added to the mixture. The mixture was stirred at a temperature of 70^0-75^0 C for 5 hours. After completion of the reaction, the mixture was washed; then, gaseous HCl was added to the mixture to remove the unreacted 3-mercapto-2-hydroxypropyl-1-isobutyl ether. The resulting triple amine was precipitated as a quaternary ammonium salt. The quaternary ammonium salt was washed twice with benzene, then treated with ammonium hydroxide and after treatment, it again turned into a converted to the triple amine. This resulted in pure 3-piperidinomethilthio-2-hydroxypropyl-1-isobutyl ether. Its physicochemical constants are given in table 1. The signals of the ^{1}H, ^{13}C NMR spectrum of 3-piperidinomethilthio-2-hydroxypropyl-1-isobutyl ether are as follows: ^{1}H NMR spectrum (fig. 5), (C_6D_6, δ, ppm): 0.84 (d., 6H, CH_3), 1.77 (m., 1H, $(CH_3)_2CH$), 2.77 (m., 1H, CHOH), 3.06 (d., 4H, CH_2O),

3.43 (m., 2H, CH_2S), 1.72, 2.81, 3.43 (m., 6H, CH_2), 4.02 (S., 1H, OH).

^{13}C NMR spectrum (fig. 6), (C_6D_6, δ, ppm): 19.14 (CH_3), 28.36 (CH_3-<u>CH</u>), 70.14 (CHOH), 78.04 (CH_2O), 37.01, 73.06,(CH_2)

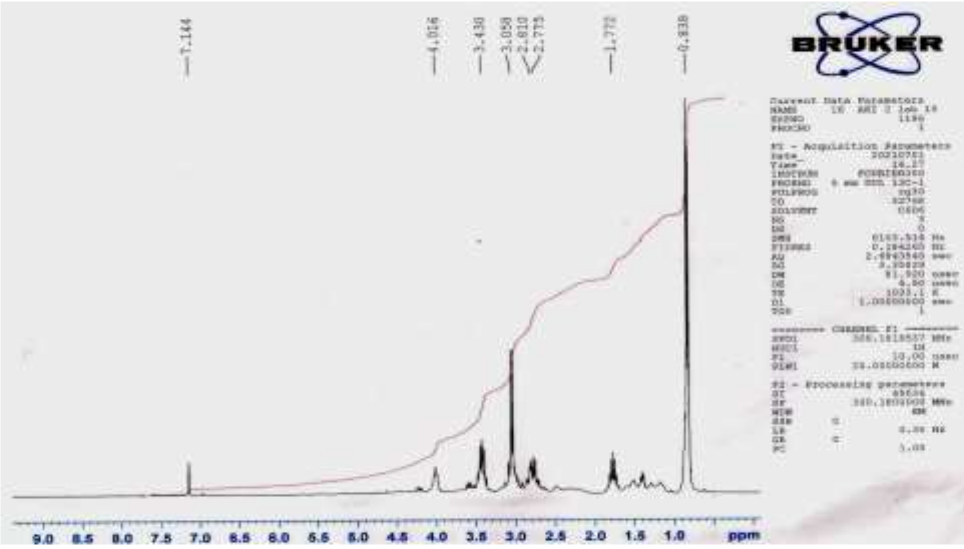


Fig. 5. ^{1}H NMR of 3-piperidinomethilthio-2-hydroxypropyl-1-isobutyl ether

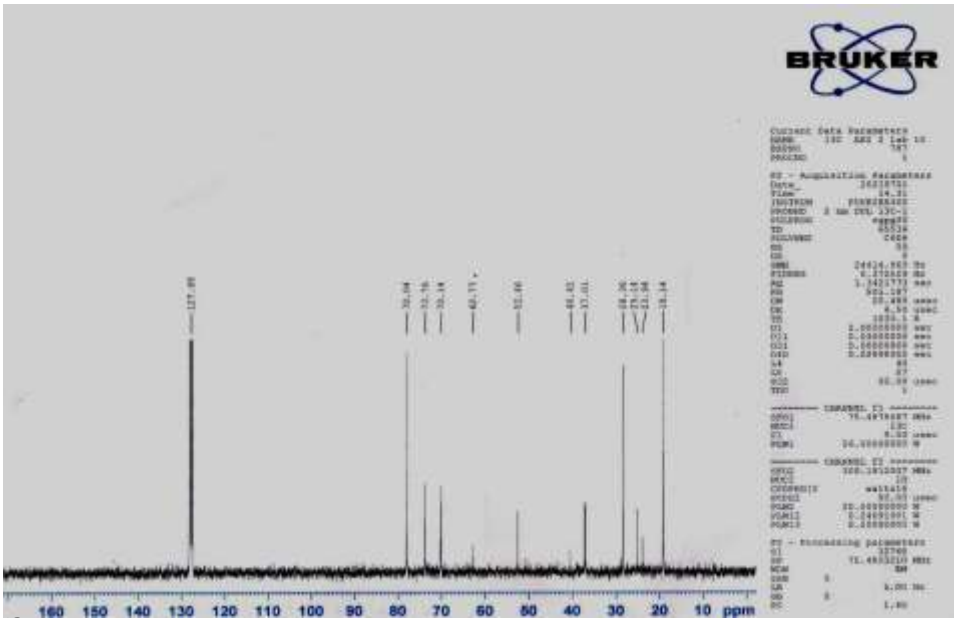


Fig. 6. ^{13}C NMR spectrum of 3-piperidinomethilthio-2-hydroxypropyl-1-isobutyl ether

The protective properties of these compounds were studied in M-12 oil in accord with methods 1, 4 and 5 according to GOST 9.054-75. Tests according to method – 1 were carried out in the humidity chamber Г-4 in the mode of periodic moisture condensation on samples of steel – 10.

First, the samples were exposed to air at a temperature of 40 ± 2^0 C and a relative humidity of 95 ± 3 % for 7 hours. Then conditions were created for moisture condensation on the samples by cooling them to a temperature lower than the temperature in the chamber by 5-10^0 C. During the tests, the samples were examined at regular intervals – from the beginning of the tests until the appearance of the first corrosion center.

According to method 4, a steel plate saturated with oil is kept in sea water for 24 hours and the corrosion process on the plate is observed.

Method 5 tests are carried out under the influence of 0,1% HBr acid solution and corrosion of the steel plate is observed within 4 hours. The test results are shown in table 2.

The best test results were obtained with compounds (III) and (IV). So, when adding 3-piperidinomethilthio-2-hydroxypropyl-1-isobutyl ether at a concentration of 1% to the lubricating oil M-12, the corrosion of a steel plate in a humid chamber is 3%, in sea water after 24 hours – 5%, the corrosion of a steel plate under the action of a 0.1% acid solution HBr – 3,5%. These results are higher than those of the standard - industrial additive urea succinimide (SIM).

Table 1. Physical-chemical characteristics of 3-mercapto-2-hydroxypropyl-1-isobutyl ether and its aminomethyl derivatives

№	Chemical formula of compounds	Yield, %	B.p., ^{0} C	n_D^{20}	d_4^{20}	Brutto formula
1	izo-C_4H_9-O-CH_2-CH-$CH(OH)$-... izo-C_4H_9-O-CH_2-CH-CH_2Cl (OH)	60	95-105 (10 mm)	1.4425	1.0465	$C_7H_{15}O_2Cl$
2	izo-C_4H_9-O-CH_2-CH-CH_2SH (OH)	51.5	155-160	1.4720	1.0156	$C_7H_{16}O_2S$
3-(I)	izo- C_4H_9O-CH_2-CH(OH)-$CH_2SCH_2N(C_2H_5)_2$	65	Non-distillable transparent liquid	1.4337	1.0548	$C_{12}H_{27}O_2NS$
3-(II)	izo- C_4H_9O-CH_2-CH(OH)-$CH_2SCH_2N(C_4H_9)_2$	62	Non-distillable transparent liquid	1.4296	1.0645	$C_{16}H_{35}O_2NS$
3-(III)	izo- C_4H_9O-CH_2-CH(OH)-CH_2SCH_2N⟨ ⟩O	63	Non-distillable Transparent liquid	1.4951	1.0869	$C_{12}H_{25}O_3NS$
3-(IV)	izo- C_4H_9O-CH_2-CH(OH)-CH_2SCH_2N⟨ ⟩	68	Non-distillable transparent liquid	1.4857	1.0579	$C_{13}H_{27}O_2NS$

Table 2. Test results of 3-mercapto-2-hydroxypropyl-1-isobutyl ether and its aminomethyl derivatives as protective additives in M-12 oil

№	Samples	Additive concentration, % (mass.)	Corrosion steel -10 (GOST 9.054-75)						
			in a humid chamber (method 1)			In sea water (method 4) for 24 hours.		When exposed to HBr (method 5) within 4 hours.	
			Time to corrosion center to appear, days.	Number of corrosion center	Corrosion, %	Number of corrosion center	Corrosion, %	Number of corrosion center	Corrosion, %
1	M-12 w/o additive	-	2	94	47	90	45	88	44
2	M-12 + izo-C_4H_9-O-CH_2-CH-CH_2SH (OH)	1.0	10	50	25	62	31	48	24
3-(I)	M-12 + izo-C_4H_9O-CH_2-CH(OH)-$CH_2SCH_2N(C_2H_5)_2$	1.0	15	25	12.5	32	16	22	11
3-(II)	M-12 + izo-C_4H_9O-CH_2-CH(OH)-$CH_2SCH_2N(C_4H_9)_2$	1.0	15	34	17	38	19	28	14
3-(III)	M-12+ izo-C_4H_9O-CH_2-CH(OH)-CH_2SCH_2N⬡O	1.0	15	8	4	11	5.5	9	4.5
3-(IV)	M-12 + izo-C_4H_9O-CH_2-CH(OH)-CH_2SCH_2N⬡	1.0	15	6	3	10	5	7	3.5
4	M-12 + SIM (standard)	1.0	15	12	6	20	10	16	8

References

1. Guliyev A.M. Chemistry and technology for oils and fuels. L.: Chemistry Publ., 1985. 312 p.
2. Foreign oils, lubricants, additives, technical fluids: International catalogue, issue 3, team of authors - Publishing house LLC Publishing center "Techinform MAI 2005, 380s.
3. Latyuk V.I., Kelarev V.I., Koshelev V.N., Korenev K.D. Sulfides of the simtriazine series as poorly soluble corrosion inhibitors. *Chemistry and technology of fuels and oils*, 2002, no. 5, pp. 23 -26.
4. Vipper A.B. On the study of the mechanism of action of additives to motor oils. *Refining and petrochemistry*. 2007, no. 1, pp. 35.
5. Allahverdiev M.A. On the reaction product of epichlorohydrin with furfural. *Russian Journal of Organic Chemistry*. 1995, vol. 31, no. 8, p.1252.
6. Abbasov V.M., Karimova N.G., Hasanov E.K. and others. Conservation oils based on salts of aromatic sulfonic acids and olefin nitration products. *Processes of petrochemistry and oil refining*. Baku, 2013, no.2 (13), pp. 14-16.
7. Balci M. Nuclear Magnetic Resonance Spektroscopy. METU PRESS. ANKARA. 2000. 458p.
8. Abbasov V.M., Mahmudova L.A., Habibullaeva R.F., Alieva L.I., Talybov A.G. Influence of anti-corrosion additives on the properties of conservation liquids based on oil I-40. *Neftepererabotka i neftechimiya - Oil refining and petrochemistry*. 2008, no. 9, pp. 34-37. (In Russian).
9. Aliev Sh.R. Investigation of nitrogen-, sulfur- and phosphorus-containing derivatives of o-hydroxy alkyl thiophenols as additives to lubricating oils. *Chemistry and Technology of Fuels and Oils*. 2012, no.3, pp. 36-39. (In Russian).
10. Sharifova S.K. Synthesis and study of epoxy esters of aromatic acids and their derivatives *Chemistry and Chemical Technology*. 2014, no. 3, pp. 27-29. (In Russian).
11. Farzaliyev V.M., Aliyev S.R., Babayi R.M., Mammadova R.F. Synthesis of aminomethyl derivatives of Mercaptomethylmorpholine and their study as a preservative additive to oils. *Azerbaijan Chemical Journal*, 2012, no. 3, pp. 13-17.

3-MERKAPTO-2-HİDROKSİPROPİL-1-İZOBUTİL EFİRİNİN AMİNOMETİL TÖRƏMƏLƏRİNİN SİNTEZİ VƏ ONLARIN SÜRTKÜ YAĞLARINA MÜHAFİZƏEDİCİ AŞQAR KİMİ TƏDQİQİ

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Xülasə: Mühərrik və mexanizmlərdə gedən elektrokimyəvi korroziyaya qarşı mübarizə xalq təsərrüfatı əhəmiyyətli məsələlərdən biridir. Texnikada istifadə olunan sürtkü yağlarının mühafizəedici effektivliyi az olduğu üçün, onlar istifadə zamanı qısa və uzun müddətli dayanmalarda mühərriklərin hissələrini korroziyadan qoruya bilmir. Bu problemin həllinin sadə və rasional yolu tərkibində effektli mühafizəedici (konservasiya) xassələrə malik olan aşqarların istifadəsidir. Bu aşqarlar sürtkü yağlarının işçi xassələrini pisləşdirmir və onlara konservasiya xassəsi verir. Sinton maddə kimi götürülmüş 3-merkapto-2-hidroksipropil-1-izobutil efirinə Mannix reaksiyası şəraitində ikili alıfatik və heterotsiklik aminlərlə təsir etməklə bir sıra aminometil

törəmələri sintez edilmişdir. 3-Merkapto-2-hidroksipropil-1-izobutil efirinin aminometil törəmələri yağlarda yaxşı həll olur və saxlanma zamanı stabildilər.
Açar sözlər: kalium hidrosulfid, korroziya, mühafizəedici aşqar, sürtkü yağları, piperidin, morfolin.

СИНТЕЗ АМИНОМЕТИЛЬНЫХ ПРОИЗВОДНЫХ 3-МЕРКАПТО-2-ГИДРОКСИПРОПИЛ-1-ИЗОБУТИЛОВОГО ЭФИРА И ИССЛЕДОВАНИЕ ИХ В КАЧЕСТВЕ ЗАЩИТНЫХ ПРИСАДОК К СМАЗОЧНЫМ МАСЛАМ

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Аннотация: Борьба с электрохимической коррозией в двигателях и механизмах – задача большого народнохозяйственного и оборонного значения. Смазочные масла, обычно используемые в технике, не обладают достаточными защитными свойствами и не способны эффективно предохранять ее от коррозии, как в процессе эксплуатации, так и при кратковременном и длительном бездействии. Одним из наиболее простых и рациональных путей решения этой проблемы является использование смазочных материалов, содержащих эффективные защитные (консервационные) присадки, которые, не ухудшая обычные рабочие свойства масел, придают им консервационные свойства. Действием на 3-меркапто-2-гидроксипропил-1-изобутиловый эфир, взятого в качестве синтона, вторичными алифатическими и гетероциклическими аминами в условиях реакции Манниха был синтезирован ряд аминометильных производных. Аминометильные производные 3-меркапто-2-гидроксипропил-1-изобутилового эфира хорошо растворяются в маслах и стабильны при хранении. Наилучшие результаты в испытаниях получены с 3-пиперидинометилтио-2-гидроксипропил-1-изобутиловым эфиром - в концентрации 1% в смазочном масле М-12 коррозия стальной пластины во влажной камере составляет 3%, в морской воде через 24 часа - 5%, коррозия стальной пластины под действием 0.1% раствора кислоты HBr – 3.5%. Эти результаты выше, чем у эталона промышленной добавки сукцинимидмочевины (СИМ).
Ключевые слова: гидросульфид калия, коррозия, защитная присадка, смазочные масла, пиперидин, морфолин.