

SYNTHESIS OF 3-PIPERIDINE-2-HYDROXYPROPYLISOBUTYL ETHER AND STUDY OF ITS ANTI-RUST PROPERTIES

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Abstract: Lubricants used in technology should have sufficient protective properties to effectively protect metal parts from rust during operation, as well as during short and long-term idle stops. One of the effective ways to solve this problem is to add effective preservative (conservation) additives to lubricants, which do not adversely affect the operating properties of lubricants and improve their preservation properties.

For the purpose of synthesis and research of effective protective additives for lubricating oils, 3-chloro-2-hydroxypropylisobutyl ether was obtained by treating isobutyl alcohol with epichlorohydrin. By adding NaOH to 3-chloro-2-hydroxypropylisobutyl ether, synthetic substance - 3,2-epoxypropylisobutyl ether was synthesized. 3-piperidine-2-hydroxypropylisobutyl ether was synthesized by treating 3,2-epoxypropylisobutyl ether with piperidine.

The structure of substance was confirmed by ^1H , ^{13}C NMR spectroscopy.

The corrosion efficiency of the compound was studied. It became clear that these compounds are more effective than the industrial additive - alkenylsuccinimide urea.

Keywords: protective additive, corrosion, rust, lubricating oils, isobutyl alcohol, epichlorohydrin, binary amines.

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Introduction

Technical progress is related to the tightening of the working parameters of machines and mechanisms, their ability to provide reliable, long-term and economical work, which, in turn, leads to aggravation of the working conditions of the lubricating oils used in them and this leads to an increase in the requirements for the quality of oils. In order to create high-quality lubricating oils that can meet modern requirements, they add organic substances, i.e. additives, to their composition. In addition to choosing high-quality raw materials, additives with different functional effects should be used in the production of lubricating oils. The synthesis of new types of additives, the study of the dependence between their functional effect and chemical structure is of great theoretical and practical importance. No matter what kind of technical equipment, it is

impossible for them to work without lubricating oil.

It is well known that rusting or corrosion in a humid atmosphere severely harms the economy of a country. Conservation and working-conservation oils containing highly effective protective additives are used as the main method of combating damage to parts of working mechanisms in industry and agriculture.

The analysis of the results of recent studies in the field of protective additives shows that alkylphenols, heterocyclic amines, organic acids and other compounds containing various functional groups and heteroatoms (N, S, etc.) are used as promising protective additives for conservation or working-preservative oils [1-7].

These compounds are surfactants (SAMs) that protect metals from electrochemical

corrosion (rusting) in an electrolyte-lubricant-metal system.

In connection with the above, 3-piperidine-2-hydroxypropylisobutyl ether was synthesized and studied in order to improve the

protective properties of lubricating oils.

The structure and composition of the synthesized compound was confirmed by ^1H , ^{13}C NMR spectroscopy and elemental analysis [8].

Experimental part

^1H and C^{13} NMR spectra of the compounds were recorded on a Bruker 300 spectrophotometer at 300 and 75 MHz, respectively. Hexamethylsilane (HMS) was used as internal standard and deuterium benzene (C_6H_6) as solvent.

For targeted synthesis, 3,2-

epoxypropylisobutyl ether was taken as starting material. 3-piperidine-2-hydroxypropylisobutyl ether was synthesized by acting on this primary substance with a double amine - piperidine [9].

The reaction was carried out according to the following scheme:

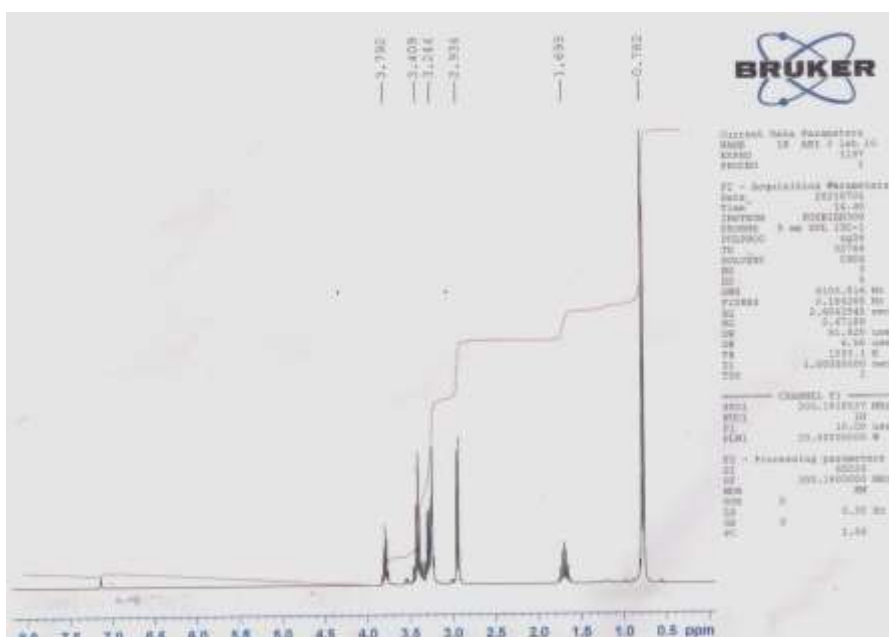
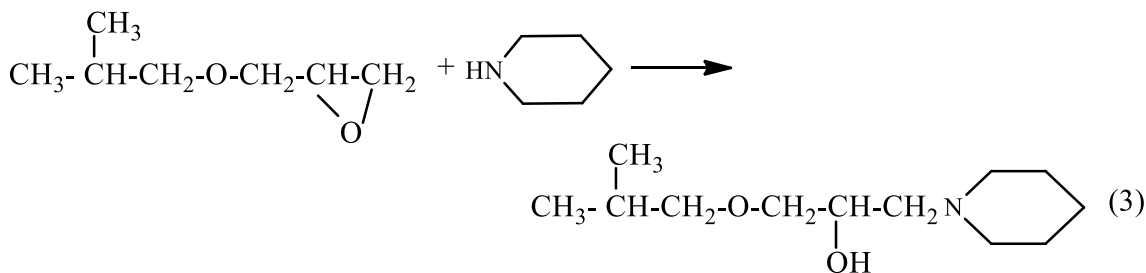
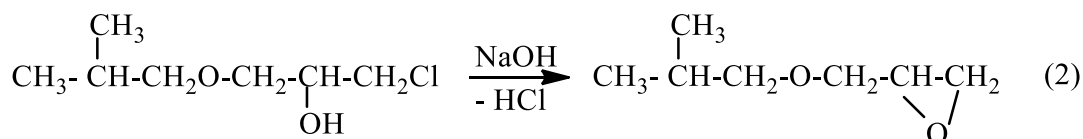
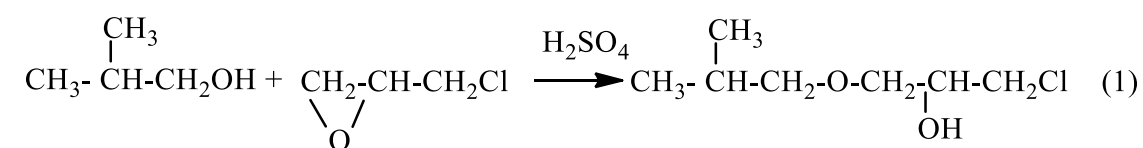


Fig. 1. ^1H NMR spectrum of 3-Chloro-2-hydroxypropylisobutyl ether

Preparation of 3-chloro-2-hydroxypropyl isobutyl ether (1). 30 g of epichlorohydrin and 36 g of isobutyl alcohol are added to a 100 ml three-necked reaction flask. Then 3 ml of 98% sulfuric acid is added dropwise to the mixture.

The mixture is stirred at a temperature of 90-95°C for 6 hours. After completion of the reaction, the mixture is extracted with toluene and the extract is washed with water, dried with CaCl_2 , and the toluene is expelled. The residue is driven off under vacuum in an oil bath.

Physico-chemical constants of the obtained substance : n_D^{20} - 1.4425 ; d_4^{20} - 1.0465 g/sm³; T_b. 95-105⁰ C; yield 60%; MR_D – calculated 33.45, found 33.16. Signals of ¹H , ¹³C NMR spectra of 3-Chloro-2-hydroxypropylisobutyl ether : NMR, ¹H spectrum (Fig. 1), (C_6D_6 , δ , ppm.): 0.78 d ($(\text{CH}_3)_2$ CH(6H), 1.7 m CH- $(\text{CH}_3)_2$ (H), 2.93 d CH_2Cl (2H), 3.24 d CH_2O CH_2 (4H), 3.41 m CHOH (H). NMR, ¹³C spectrum (Fig. 2), (C_6D_6 , δ , ppm.) : 18.94($(\text{CH}_3)_2$ CH-, 28.18 CH($(\text{CH}_3)_2$, 46.06 CH_2Cl , 72.89 CH_2O CH_2 -, 78.03 CHOH .

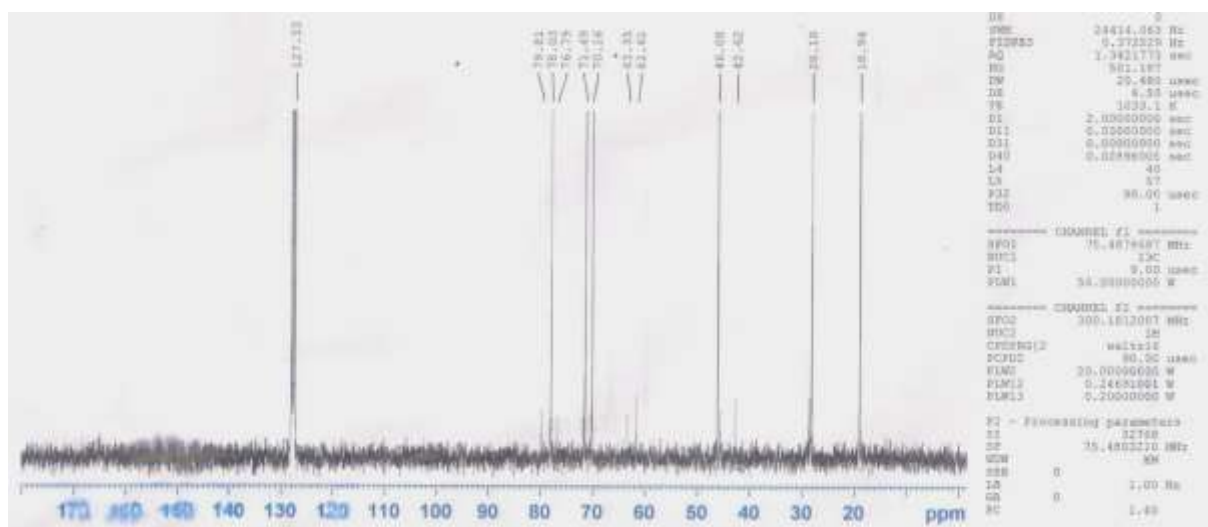


Fig. 2. ¹³C NMR spectrum of 3-Chloro-2-hydroxypropylisobutyl ether

Synthesis of 3,2-Epoxypropylisobutyl ether (2). To a 100 ml three-necked reaction flask equipped with a mechanical stirrer, reflux condenser and thermometer, add 10 g (0.07 mol) of 3-chloro-2-hydroxypropylisobutyl ether and 2.5 g of NaOH to 30 ml of benzene (dissolve 2.5 g of NaOH in 6 ml of water) 29% is given in the form of a solution. The reaction mixture is stirred at a temperature of 75-80°C for 5-6 hours. The mixture is extracted with benzene, the extract is washed with water, dried with

Na_2SO_4 , and the benzene is expelled. The residue is expelled in a vacuum in an oil bath. T_b. = 100-101⁰ C, (10 mm c.st.) ; yield : 54%, (5 g) ; n_D^{20} - 1.4145 ; d_4^{20} - 0.9242 g/sm³. Chemical formula of the substance $\text{C}_7\text{H}_{14}\text{O}_2$; calculated, % : C - 64.61 ; H - 10.85 ; found, % : C - 64.54 ; H - 10.43

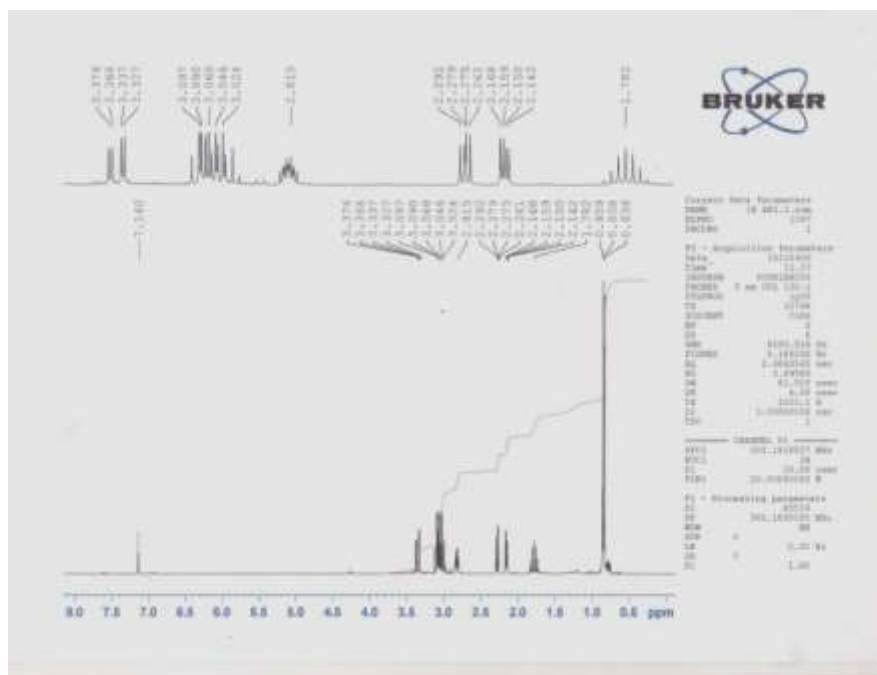


Fig. 3. ^1H NMR spectrum of 3,2-Epoxypropylisobutyl ether

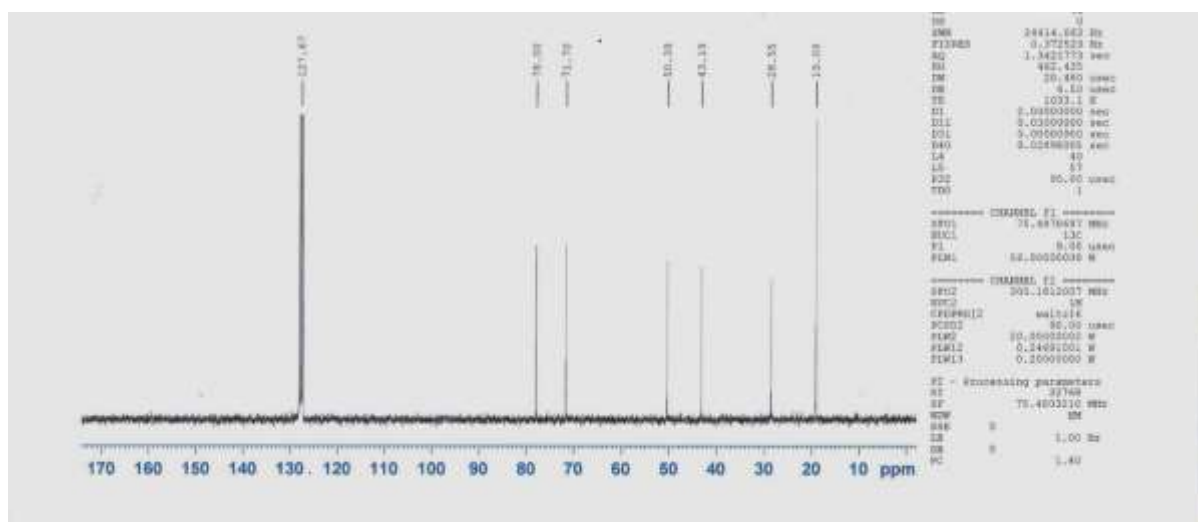


Fig. 4. ^{13}C NMR spectrum of 3,2-Epoxypropylisobutyl ether

Synthesis of 3-Piperidine-2-hydroxypropylisobutyl ether (3). 6 g (0.07 mol) of 3,2-epoxypropylisobutyl ether and 30 ml of benzene are added to a 100 ml three-necked reaction flask. Then, 4 g (0.04 mol) of piperidine is added dropwise to the mixture. At this time, the temperature of the mixture rises to 35°C. The mixture is stirred at a temperature of 75-80°C for 6 hours. After the reaction is complete, the mixture is extracted with benzene, the extract is washed several times with water, dried with Na_2SO_4 , and the benzene is expelled.

The final product: T_b = 109-110°C, (6 mm c.st.) ; yield : 64%, (4 g) ; n_D^{20} – 1.4665 ; d_4^{20} – 0.9797 g/sm³. Chemical formula of the substance $\text{C}_{12}\text{H}_{25}\text{O}_2\text{N}$.

Calculated, % : C – 54.19 ; H – 16.12 ; O – 20.64 ; N – 9.03

Found, % : C – 54.34 ; H – 15.63 ; O – 20.14 ; N – 10.01

Signals of ^1H , ^{13}C NMR spectra of 3-piperidine-2-hydroxypropylisobutyl ether: NMR, ^1H spectrum (Fig. 5) (C_6D_6 , δ , ppm.):

0.81d (6H, (CH₃)₂); 1.2 m (2H, -CH₂-CH₂-CH₂-); 1.78 m (H, -CH-);

1.37 m (4H, -CH₂-CH₂-CH₂-); 2.28 t (4H, N-CH₂); 3.10 d (2H, -CH₂-N-);

3.4 d (2H, -CH₂-O-); 3.79 s (OH); 3.86 t (H, -O-CH-).

NMR,

¹³C spectrum (Fig. 6) (C₆D₆, δ, ppm.):

25.97 (-CH₂-CH₂-CH₂-); 28.46 (-O-CH-); 54.81 (N-CH₂); 62.49 (CH₂-N-);

66.49 (-CH₂-O-); 74.01 (O-CH-).

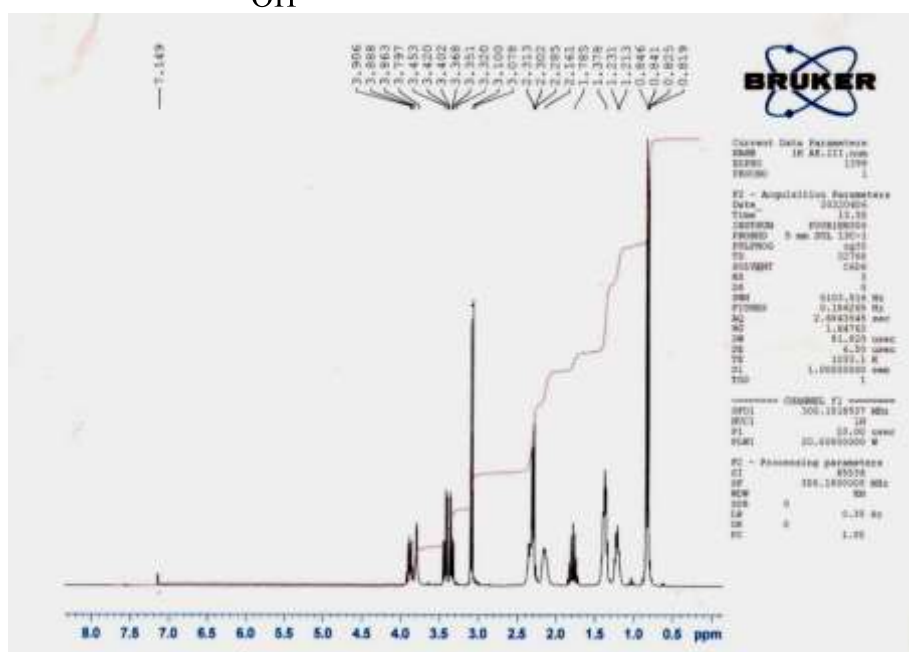


Fig. 5. ¹H NMR spectrum of 3-Piperidine-2-hydroxypropylisobutyl ether

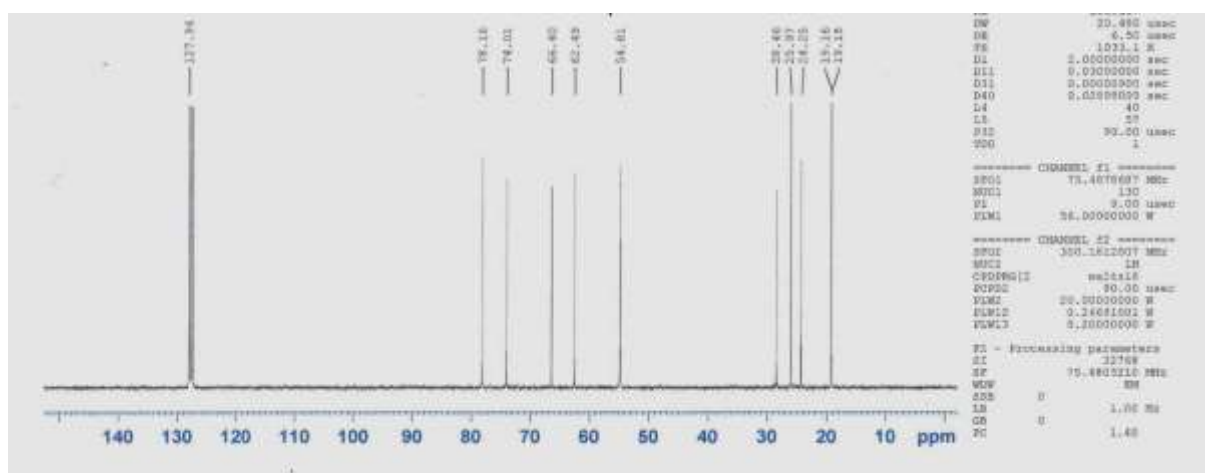


Fig. 6. ¹³C NMR spectrum of 3-Piperidine-2-hydroxypropylisobutyl ether

It is known, some organic compounds containing N, O and S have high adsorption activity, passivating them in contact with metal and showing effective protective properties [10-12].

Tests of 3-piperidine-2-hydroxypropylisobutyl ether based on 3,2-epoxypropylisobutyl ether as protective anti-rust additives were conducted and evaluated in the humidity chamber (Г-4) included in the complex research system according to GOST 9.054-75, under the influence of sea water and 0.1% solution of HBr acid. Steel-10 plates are ground, polished, washed with hexane or heptane, cleaned with alcohol and dried before testing, and the surface of the plates is not touched by hand. Then the anti-rust additive is added to the oil at a concentration of 1% and mixed.

Steel plates are immersed in this additive oil for 1 minute and hung in the open air for 1 hour. Then Г-4 is placed in a humidity chamber and corrosion is observed and evaluated.

Tests according to the 1st method were carried out in the humidity chamber Г-4 on samples made of steel (steel-10) in the mode of periodic condensation of moisture. First, the samples are exposed to a regime consisting of a temperature of $40 \pm 2^\circ$ and a relative humidity of $95 \pm 3\%$ for 7 hours. Then conditions are created for moisture condensation on the samples (by cooling them to a temperature lower than the chamber temperature, i.e. $5-10^\circ\text{C}$). During the test, from the start of the

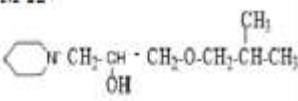
process to the appearance of the first corrosion center, the samples are visually inspected at regular intervals.

In the 4th method, a steel plate immersed in oil is kept in sea water for 24 hours, and the corrosion process on the steel plate is observed.

Tests according to the 5th method are carried out under the influence of a 0.1% solution of HBr acid. So, for the test, 2 glasses are taken, one is filled with added oil, and the other is filled with a 0.1% solution of HBr acid. The steel plates are first immersed in the solution of HBr acid for 1 second at room temperature, then taken out and immersed in a beaker containing added oil 12 times for 1 minute and suspended in the air for 4 hours. Then the corrosion on the steel plate is reviewed and evaluated. The results of the tests are given in the table.

The results of the tests revealed that when 3-piperidine-2-hydroxypropylisobutyl ether is added to M-12 lubricating oil at a concentration of 1%, the anti-rust property of the oil increases dramatically. In the presence of 3-piperidine-2-hydroxypropylisobutyl ether, corrosion in a humidity chamber begins after 20 days and corrosion on a steel plate is 3.5%, corrosion after 24 hours in seawater is 4.5%, corrosion after 4 hours under the influence of a 0.1% solution of HBr acid is 3%. In comparison, the results of 3-piperidine-2-hydroxypropylisobutyl ether are higher than those of the benchmark industrial additive alkenylsuccinimide urea (SIM).

Table. Test results of 3-piperidine-2-hydroxypropylisobutyl ether as protective anti-rust additive in M-12 oil

	Sample names	Additive viscosity, %	Humidity chamber (method-1)			Sea water 24 hours (method-4)		HBr effect 4 hours (method-5)	
			Duration of the onset of corrosion foci, days	The number of corrosion foci	Corrosion, %	The number of corrosion foci	Corrosion, %	The number of corrosion foci	Corrosion, %
1	M-12 oil without additive	-	4	80	40	90	45	88	44
5	M-12+ 	1.0	20	7	3.5	9	4.5	6	3
6	M-12 + SIM (standard)	1.0	15	12	6	20	10	16	8

Conclusion

Thus, it was determined that 3-piperidine-2-hydroxypropylisobutyl ether has high anti-rustprotection efficiency. Based on the results of the tests, it can be said that the synthesized 3-

piperidine-2-hydroxypropylisobutyl ether can be recommended for extensive testing for the purpose of creating working-preservative oils.

References

1. 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**, p. 23 -26.
2. Shekhter Yu.N., Krein S.E., Teterina D.N. Oil-soluble surfactants. M.: Chemistry, 1978. p. 161.
3. Vipper A.B., Vilenkin A.V., Geisner D.A. Foreign oils and additives. M.: Chemistry, 1981, p. 103.
4. 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 Chemistry Journal*, 2012, **no. 3**, p. 13-17.
5. Urinov U.K., Maksumova O.S., Abdulmalikova H.B. On the reaction between urea and epichlorohydrin. *Austrian Journal of Technical and Natural Sciences - Vinna*. 2016, **no. 3-4**. p. 141-145.
6. Farzaliyev V.M., Aliyev Sh.R., Babayi R.M., Guliyeva Q.M. Synthesis and research of new protective additives based on binary heterocyclic amines. *Journal of Qafqaz University*, 2016, **no. 1**, p. 16-20.
7. Sharifova S.K. Synthesis and study of epoxy esters of aromatic acids and their derivatives. *Chemistry and Chemical Technology*. 2014, **no. 3**, p. 27-29 (In Russian).
8. Balci M. Nuclear Magnetic Resonance Spektroskopy. METU PRESS. ANKARA. 2000. 458 p.
9. Heravi M.M., Behbahani F.K., Oskooie H.A., Bamoharram F.F. $H_{14}[NaP_5W_{29}MoO_{11}]$: a Novel and Useful Catalyst for Aminolysis of Epoxides with Amines under Solvent-Free Conditions. *Chinese Journal of chemistry*, 2008, **Vol. 26(12)**, p. 2150-2154.
10. Farzaliyev V.M., Aliyev Sh.R., Babai R.M., Kulieva G.M. Aminomethyl derivatives of mercaptomethylpiperidine as protective additives for lubricating oils. *Journal of Oil Refining and Petrochemistry*, 2015, **no. 7**, p. 44 -45.
11. Abbasov V.M., Kerimova N.G., Gasanov E.K. et.al. Preservation oils based on salts of aromatic sulfonic acids and olefin nitration products. *Petrochemical and oil refining processes*. 2012, **Vol. 13 (2)**, p. 14-16.
12. Farzaliyev V.M., Aliyev Sh.R., Babai R.M., Mammadova R.F., Guliyeva G.M., Mammadov A.M., Eivazova G.Sh. Synthesis of aminomethyl derivatives of 3-mercapto-2-hydroxypropyl-1-isobutyl ether and their study as protective additives to lubricant oils. *Chemical Problems*, 2023, **no. 1**, p. 48-56.