Published Date: - 30-01-2025
Page No: - 93-100

OBTAINING CORROSION INHIBITORS BASED ON HETEROCYCLING REACTIONS OF POLYETHYLENEPOLYAMINE WITH C16-C18 FATTY ACIDS

Usmonova Yulduz Sheralievna
Tashkent Institute of Chemical Technology, Associate professor of the department, Uzbekistan

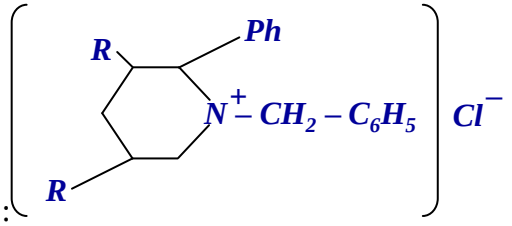
Roziev Shokhrukh Farkhodovich
Tashkent Institute of Chemical Technology, Doctoral student, Uzbekistan

Kadyrov Hassan Irgashevich
Tashkent Institute of Chemical Technology, Professor of the department, Uzbekistan

ABSTRACT
Today, one of the important tasks of the chemical industry is to create new corrosion inhibitors for these structural materials and evaluate the effectiveness of their use. Extensive experience has been accumulated in the preparation of polyfunctional heterocyclic compounds from high-tonnage olefins, glycols, amines, etc., capable of preventing the decomposition of materials in aggressive environments [1, 2].

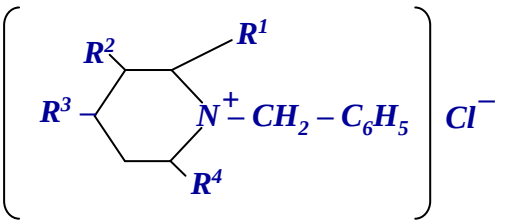
KEY WORDS
High-tonnage olefins, glycols, amines.

INTRODUCTION
Today, one of the important tasks of the chemical industry is to create new corrosion inhibitors for these structural materials and evaluate the effectiveness of their use. Extensive experience has been accumulated in the preparation of polyfunctional heterocyclic compounds from high-tonnage olefins, glycols, amines, etc., capable of preventing the decomposition of materials in aggressive environments [1, 2].
A number of works devoted to the creation of hydrogen sulfide corrosion inhibitors based on petrochemical products were carried out by the school of Professor D.L. Rakhmankulov [3]. Effective reagents based on pyridine salts were identified



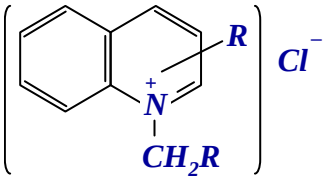
R=CH_3; C_2H_5; C_3H_7; C_4H_9; C_5H_{11}

2-Aryl-3,5-dialkylpyridiniumbenzyl chlorides



R^1=R^4 = CH_3; R^2=R^3=CH_3 or R^1=R^4=CH_3; R^2=C_2H_5; R^3=CH_3 or R^1=R^4= C_3H_7; R^2=R^3= CH_3; or R^1=R^4=C_3H_7; R^2=C_2H_5; R^3=CH_3

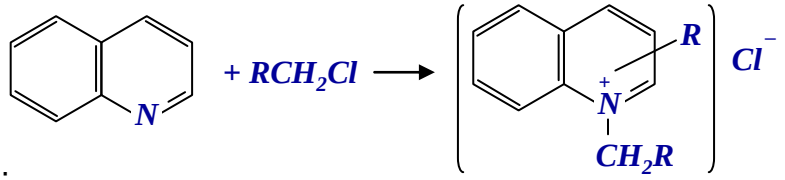
2,3,4,6-tetraalkylpyridiniumbenzyl chlorides



R= $C_{10}H_{21}$-$C_{20}H_{41}$;

alkylquinolinium chlorides

The quaternary salt of quinoline showed the maximum activity



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Its use ensured a reduction in the corrosion rate of steel 20 by an equal or greater amount in a 25% hydrochloric acid solution.

The use of nitrogen-containing cyclic compounds - alkyl imidozolines - as corrosion inhibitors for a wide range of petrochemical processes has been proposed [4,5]. Carbonic acids, which are the initial raw materials for the production of alkylimidazolines, are obtained by direct oxidation of paraffins with atmospheric oxygen.

In the conditions of our republic, this important raw material can be obtained by separating individual components from a mixture of synthetic fatty acids, a secondary product of the oil and fat industry. Carboxylic acids are usually separated C_{10}-C_{14}, C_{14}-C_{16}, and C_{16}-C_{20} fractions by distillation. Both the acids themselves, their cubic residues, and their amides have been studied as acid corrosion inhibitors. One such secondary product is soapstock - a refined (clarified) product obtained as a result of alkaline purification of vegetable oils and fats in the oil refining industry. It has a variable, complex composition, depending on the nature of the oils and fats, the methods of their extraction and purification, and the conditions of the technological process of processing [6].

Soapstock consists of an aqueous solution of soap, oil, phosphorus compounds, dyes, mineral and mechanical additives. The approximate composition of soapstock obtained from the processing and purification of cottonseed oil (%): fats - 8-50 (including soap - 8-30, neutral oils - 1-20); water and non-decomposable components - 50 - 92 (unreacted NaOH, NaCl, as well as dyes, phosphatides, proteins, carbohydrates, bentonite).

To separate the bright fatty acids from the soapstock, it is treated with mineral acids or alkalis before using the distillation method. Fatty acids extracted from salomas and fatty acid soapstocks are used in the production of soap, glycerin and stearic acid.

The sapstock, a secondary product of the Kattakurgan oil and fat complex in the Samarkand region, used in the research, contains 13 types of fatty acids, 10 of which are saturated (34.3%) - $C_9H_{19}COOH$, $C_{13}H_{27}COOH$, $C_{15}H_{31}COOH$, $C_{16}H_{33}COOH$, $C_{17}H_{35}COOH$, $C_{19}H_{39}COOH$, $C_{21}H_{43}COOH$, $C_{22}H_{45}COOH$, $C_{23}H_{47}COO_N$, $C_{24}H_{49}COO_N$, 3 are unsaturated - $C_{16}H_{31}COOH$, $C_{17}H_{33}COOH$, $C_{17}H_{31}COOH$, and the main ones are palmitic, oleic and linoleic acids.

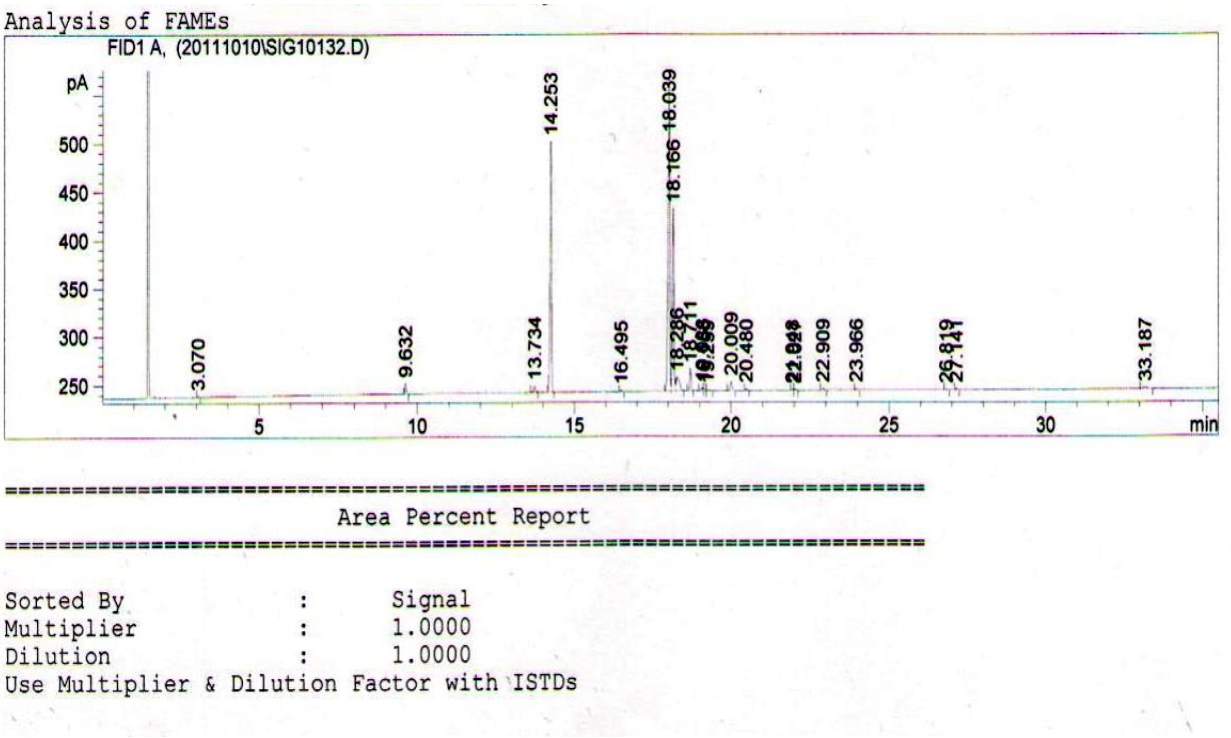
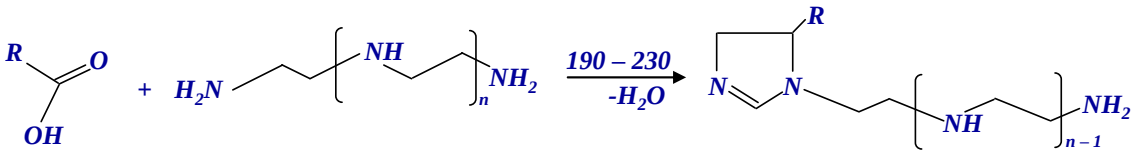


Figure 1. Gas-liquid chromatography of fatty acids

Corrosion inhibitors were obtained from a mixture of polyethylenepolyamine (PEPA) and fatty acids - soapstock - by known methods [7]: a mixture of fatty acids is placed in a reactor equipped with a mechanical stirrer, dropping funnel, thermometer, and Dyna-Stark nozzles, heated, dissolved, and mixed. A homogeneous mass is formed as the reactor temperature rises to 60 °C. Depending on the moisture content of the soapstock, heating is continued for 2 - 2.5 hours. Then, PEPA is rapidly fed into the reactor through a dropping funnel. The reaction mixture is then heated at a temperature of 130-150 °C for 3-3.5 hours, and the reaction and soapstock water are collected in a Dyna-Stark collector. During heat treatment, the maximum

temperature of the mixture is maintained at 230 °C for one hour. In this, complete separation of water is carried out.

The synthesis of imidozoline derivatives based on a mixture of fatty acids and PEPA is carried out according to the following reaction:



It has been proven that imidozoline synthesis proceeds via a linear amide formation step. Depending on the reaction conditions, monoamides and diamides of fatty acids are formed in the first step, which ensure the formation of the imidozoline ring.

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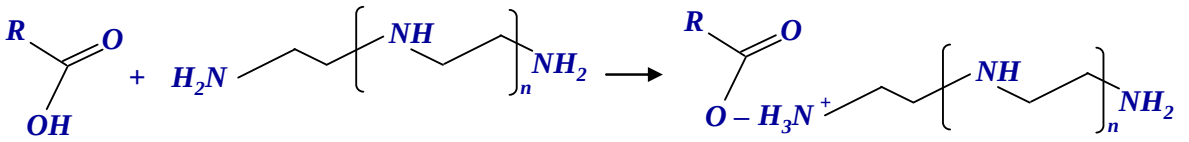
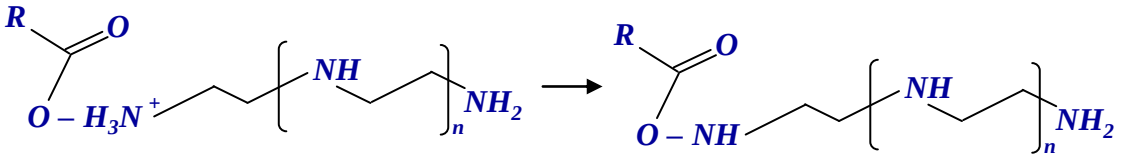
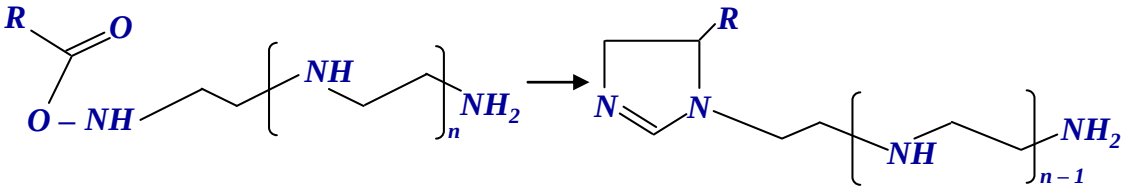


Stage 2. Separation of water from ammonium salts of carbonic acid and formation of amides:



Stage 3. Cyclization of carboxylic acid amides and formation of imidozoline derivatives:



In order to determine optimal conditions for the synthesis of imidozoline derivatives based on a mixture of fatty acids and ethylenediamine, the effect of temperature was studied in the range of 130-230 °C, the research was carried out in two stages. The temperature of the initial reagents after loading them into the reactor flask was 160°C, and the reaction was carried out for 3 hours with the collection of reaction water in the Dean-Stark nozzles, as described in Chapter 2 of the dissertation.

Then the reaction is continued at a temperature of 190 °C for 8 hours. The adduct formed at this stage of the synthesis is a brown liquid with a white precipitate consisting of up to 50%

acid linear amides. Dewatering is also carried out at a temperature of 230 °C, a homogeneous liquid of brown color is formed, and no sediment remains.

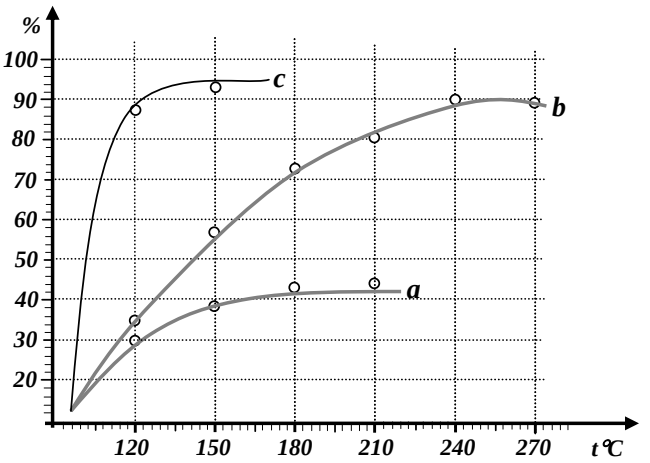


Figure 2. Dependence of the yield of imidozoline formation on temperature
a) after the first stage of two-stage heat treatment; b) after the second stage of two-stage heat treatment; c) in the presence of an acidic catalyst

In the next step, the amount of water of reaction that was released was determined and compared with the calculated amount (the calculated amount was taken relative to the complete conversion of imidazoline).

Table 2

Amount of water released in imidozoline synthesis

Reaction conditions	Separated water of reaction	Calculated water separation
after the first stage of two-stage heat treatment	4.3	7.2
after the second stage of two-stage heat treatment	4.5	7.2
after heat treatment	8.1	7.2

The comparative ratios of the reaction product and the calculated amount of water (Table 2) confirm that the initial reagents are produced with high conversion to the target imidozoline. Although the ratios are high when thermal treatment is carried out at 190 °C, at 230 °C, the conversion increases sharply, leading to an increase in the yield of imidoline.

Another method of determining the composition of reaction products is the use of IR-spectroscopy. Figure 3 shows the IR-spectra of the products obtained from the mixture of fatty acids and PEPA.

Under all conditions of the synthesis, absorption lines characteristic of linear amides at 1605 cm^{-1} C = N-bond and absorption lines characteristic of C = O-bond at 1650 and 1550 cm^{-1} were observed

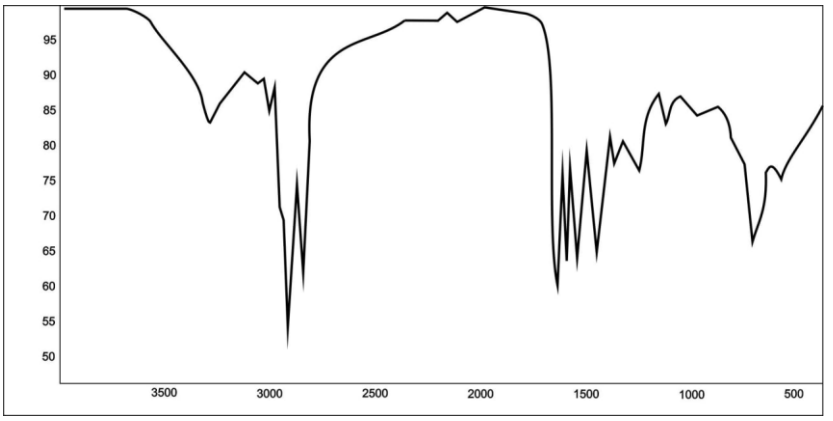


Figure 3. IR-spectrum of the obtained sample

In the IR spectrum of the obtained sample (Figure 3), absorption lines characteristic of the C=N bond are observed. The intense absorption of the C=N bond characteristic of the imidazoline ring is greater in the sample obtained by acid catalysis. Here, we see that the absorption intensities for the C = N and C = O bonds are interrelated, with the intensity of one bond increasing while the intensity of the other decreases. By comparing the C = N bond intensities in the IR spectra of the samples under different conditions, it is possible to prove the presence of imidozoline derivatives. After calculations, it was determined that the amount of imidozoline derivatives in the samples, when subjected to thermal treatment, was 80 - 85%.

The determination of the level of corrosion protection of inhibitors based on imidazoline derivatives, conventionally called IIK-D, was carried out on steel samples of grade St.20 using gravimetric and potentiometric methods. The inhibitor dose was determined in the range of 20 - 40 mg/l (Table 3). The experiments were conducted for 24 hours at room temperature in two-phase systems: gas condensate-salt artificial solution and oil-salt artificial solution. The analyzed media were enriched with hydrogen sulfide for 10 minutes. The composition of the mineralized salt solution consists of KCl (163 g/l) + CaCl2 ·2H2O (34 g/l) MgSO4 (0.14 g/l). Table 3 shows the results of determining the level of corrosion protection of St.20 grade steel by inhibitors based on imidozoline derivatives.

Table 3

Results of determination of corrosion protection level of St.20 grade steel of the inhibitor based on imidozoline derivatives

Environment of experiments	Loss of mass, g	Corrosion rate $g/m^2 \cdot h$	Protection level, %
20 mg/l «ИИК-D»			
Control	0,0255	0,0331	

H_2S +saline solution+ 70 ml gas condensate	0,0004	0,00519	84,3
Назорат	0,0012	0,01557	-
H_2S +saline solution + 70 ml oil	0,0013	0,01428	91,6
Control	0,0107	0,1388889	-
H_2S + saline solution	0,00115	0,0149273	89
30 mg/l «ИИК-D»			
Control	1,54235	0,4053	-
1:2 = water: saline solution with H_2S	0,3953	0,1020	74,8
Control	0,2985	7,8483	-
H_2S saline solution + 70 ml oil	0,11565	2,738	65,1
Control	0,61865	7,5736	-
H_2S + saline solution	0,095	2,5067	66,9
30 mg/l «ИИК-D»			
Control	0,00306	0,3952	-
1:2 = water: saline solution with H_2S	0,0053	0,00365	90,7
Control	0,0051	0,196	-
H_2S saline solution + 70 ml oil	0,00215	0,02791	85,8
Control	0,001	0,01298	-
H_2S + saline solution	0,00015	0,00128	90,1

Table 3 shows the results of the temperature dependence of the degree of protection of the acidic corrosion inhibitor IIK-D, and it can be seen that the degree of corrosion protection of steel grade St.20 is 90%.

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