

AZERBAIJAN REPUBLIC

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ABSTRACT

of the dissertation for the degree
of Doctor of Sciences

**OBTAINING CYCLOALKYLPHENOL DERIVATIVES
MODIFIED BY ALKYLIMIDAZOLES AND STUDY OF
ANTIOXIDANT PROPERTIES**

Specialty: 3349.01 - Chemistry and technology of gas
conversion processes

Field of science: Technology

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Baku – 2023

The work was performed at the laboratory "Chemistry and technology of alkylphenols" of the Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev of the Ministry of Science and Education of the Republic of Azerbaijan


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GENERAL CHARACTERISTICS OF THE WORK

Relevance of the topic and the degree of elaboration.

Countries with broad economic opportunities along with the production of metal structures, machine parts, polymers, oils, rubbers and fuels, they prefer to increase their service life and improve their quality properties. In order to increase their resistance to corrosion, aging, destruction, abrasion, an infinite number of inhibitors, stabilizers, antioxidants, additives are produced in the industry. However, all this does not last in the face of the ever-increasing demands of the industry. These requirements include reducing the increase in emissions into the biosphere (gases, polymeric materials, corroded metal parts), the development of new compact technologies and the implementation of more cost-effective processes.

For this reason, more recently, the acquisition and use of chemical compounds with multifunctional properties, which at the same time improve several properties (synergism) of the object to which it is applied, is becoming more preferred.

The C₅-fraction obtained during the pyrolysis of low-octane gasoline has not yet found its effective use. Involvement of C₅-fraction, one of the main products of gas chemistry, in the research object is of great ecological and economic importance.¹ The technology of the process of obtaining 1- and 3-methylcyclohexenes from the Dils-Alder reaction with ethylene of the C₅-fraction, consisting mainly of isoprene and piperilen, has been developed at our institute.² One of the important issues is to study the alkylation reactions of these products with *para*-cresol in the new catalytic system, to determine the derivatives and compositions of the obtained 2-methylcyclohexyl-4-methylphenols with alkylimidazoles and to determine new applications.

In this regard, the dissertation is devoted to a topical issue - the

¹ Gas chemistry (textbook)/ V.M.Abbasov [and others]. – Baku: East-West Publishing House, – 2015. – 464 p.

² 90 years of development of IPCP: from the experience of the past - to the projects of the future/Chief scientific editor is academician Vaqif Abbasov. – Baku: Science, –2018. – 764 p.

study of aminomethylation reactions of methylcyclohexyphenols with formaldehyde and aminoethylnonylimidazole obtained from the catalytic alkylation of *para*-cresol with cycloolefins of various structures, acquisition and testing of oxyethylated nonylphenols and cycloalkylphenols modified by alkylimidazoles.

Object and subject of research. The object of research is the study of the effect of *para*-cresol, methylcyclohexanes of different chemical structures, catalysts containing cationite and zeolite, the direction, yield and selectivity of various factors in cycloalkylation reactions; the subject of the research is the production of Mannix bases from the interaction of the obtained 2(methylcyclohexyl)-4-methylphenols with alkylimidazolines and their testing in various fields.

Objectives and tasks of the research. The aim is to study the methylcyclohexenes of different structures obtained on the basis of gas chemistry products, the aminomethylation reactions of the obtained space-difficult cycloalkylphenols with aminoethylnonylimidazole, as well as the preparation of alkylimidazolines with oxyethylated modified nonylphenol. The following tasks were performed to achieve the goal:

- study of catalytic alkylation reactions of *para*-cresol with 1- and 3-methylcyclohexenes, cyclodimers of isoprene in a pilot device with intermittent and uninterrupted operation;
- study of aminomethylation reactions of space-difficult methylcyclohexylphenols with formaldehyde and aminoethylnonylimidazole (AENI);
- obtaining modified samples of 2-methylcyclohexyl-4-methyl-, 4-methylcyclohexyl- and 2,6-dimethyl-cyclohexyphenols with alkylimidazoline;
- and testing of new conservation fluids from the modification of oxyethylated *para*-nonylphenol with alkylimidazoline.

Research methods. Scientific research was carried out in the laboratory and semi-industrial facilities created on the basis of the technological scheme provided by us.

The accuracy of the scientific results obtained in the dissertation was proved by various modern physical research

methods (IR-, NMR-, scanning electron microscope (SEM), X-ray diffractograms).

The main provisions of the defense:

- cycloalkylation reactions of *para*-cresol with methylcyclohexene in a new catalytic system were carried out, kinetic regularities and mechanism of reactions were studied;
- Mannix bases were synthesized from the interaction of the obtained space-difficult cycloalkylphenols with aminoethylnonylimidazole;
- complex compounds based on methylcyclohexylphenols were tested in the process of oligomerization of ethylene as a ligand to heterogeneous metal complex catalytic precursors;
- obtained Mannix bases have been tested as a high temperature resistant antioxidant in CKN-26 nitrile rubber and M-8 engine oil;
- composites were obtained from modification of space-difficult cycloalkylphenols and oxyethylated nonylphenol with alkylimidazole, modification of alkylimidazole with oxyethylated nonylphenol was carried out in the pilot plant;
- composites of alkylimidazole-based modifications were studied for their anti-corrosion inhibitor properties in CO₂ environment, their effect against sulfate-reducing bacteria and tested as a surfactant.

Scientific novelty of the research:

- for the first time, the interactions of *para*-cresol with 1- and 3-methylcyclohexenes, isoprene cyclodimers in the presence of zeolite-Y catalysts impregnated with KU -23 and orthophosphate were studied, the effect of various kinetic parameters (temperature, time, molar ratios of initial components, amount of catalyst, volume and velocity) on the yield and selectivity of the target product was studied;
- aminomethylation reactions of space-difficult and para-cycloalkylphenols with aminoethylnonylimidazole were carried out and Mannix bases with 20 new chemical structures were obtained;
- interaction reactions of natural petroleum acid with polyethylene polyamine were first performed in nitrogen.
- new types of composites were obtained from modifications of space-difficult and para-methylcyclohexylphenols, oxyethylated nonylphenols with alkylimidazoles;

- 2 Azerbaijani and 2 Eurasian patents were obtained as a result of scientific research.

Theoretical and practical significance of the research. The theoretically substantiated fields of application of synthesized space-difficult cycloalkylphenols and their alkyylimidazoles and Mannix bases, modified composites have been determined.

2-Methylcyclohexyl-4-methylphenol is a raw material for the production of Bisalkofen-MTSP thermostabilizer, which is widely produced and used in industry. In addition, 2-methylcyclohexyl-4-methylphenols have been used as ligands in catalytic precursors used in the oligomerization of ethylene.

The aminomethylation products of 2-methylcyclohexyl-4-methylphenols with paraform and aminoethylnonylimidazoline have been tested as a high temperature resistant antioxidant in M-8 engine oil. In addition, the obtained Mannix bases were tested as an antioxidant for CKN-26 nitrile rubber, with positive results.

Composites obtained from the modification of methylcyclohexylphenols and oxyethylated nonylphenols with alkyylimidazolines have been tested as conservation against corrosion of metals and as a CO₂ corrosion inhibitor. The tests were compared with known inhibitors.

Modifications of oxyethylated nonylphenol with alkyylimidazoline have been tested as surfactants. The obtained products have shown high efficiency.

Modification of oxyethylated nonylphenol with alkyylimidazole (ONP-AIM) was carried out in a pilot plant at "Tural 110" scientific-production enterprise in Sumgayit. Technical and economic indicators of the process have been calculated. According to preliminary estimates, the cost of ONP-AIM was determined to be AZN 2579/ton.

Approbation and application.

42 scientific works on dissertation work, including 22 articles (7 without co-authors), theses of 15 reports at conferences of different levels, 1 book were published and 4 patents were obtained.

The main results of the work were published in the following journals: "Processes of Petrochemistry and Oil Refining", "The work

of higher education institutions. Chemistry and chemical technology”, “ScientificNet. Publisher in Materials Science & Engineering”, “Oil refining and petrochemistry. Scientific and technical achievements and best practices”, “The world of petroleum products. Oil companies bulletin”, “Problems of Chemistry”, “Scientific Collection of the National Aviation Academy”, Nakhchivan State University. Scientific works. “Natural and medical sciences series”, “Scientific and pedagogical news of Odlar Yurdu University”, “Mechanics and Industrial Engineering. Journal of Baku Engineering University”, Sumgait State University. Scientific news. “Department of Natural and Technical Sciences” and “News of Azerbaijan Higher Technical Schools”.

The results of the dissertation were also discussed at the following scientific conferences and published in the conference materials:

Materials of the 7th International Scientific and Technical Conference. “Techniques and technology of petrochemical and oil - gas production” (Omsk, April 24-28, 2017), International scientific conference on "Actual problems of modern natural sciences" dedicated to the 94th anniversary of national leader Heydar Aliyev (Ganja, May 04-05, 2017), International scientific-technical conference on "Petrochemical synthesis and catalysis in complex condensed systems", dedicated to the 100th anniversary of academician B.G. Zeynalov (Baku, June 29-30, 2017), XIII International Scientific and Practical Conference “New polymer composite materials” (Nalchik, July 5-9, 2017), Republican scientific-technical conference "Fuels, fuel components, special fluids, oils and additives" dedicated to the 90th anniversary of S.A. Sultanov (Baku, October 3, 2017), International scientific conference "Functional monomers and special polymer materials: polymers, perspectives and practical views" (Sumgayit, November 15-16, 2017), International scientific conference on "Actual problems of modern natural and economic sciences" dedicated to the 95th anniversary of H.Aliyev (Ganja, May 4-5, 2018), XIV International Scientific and Practical Conference “New polymer composite materials” (Nalchik, 4-8 July 2018), XII International Conference of

Young Scientists on Petrochemistry (Zvenigorod, September 17-21, 2018), International scientific-practical conference dedicated to the 110th anniversary of academician V.S. Aliyeva. “Innovative prospects for the development of oil refining and petrochemistry” (Baku, October 9-10, 2018), Materials of the scientific conference “Naghiyev readings” dedicated to the 110th anniversary of academician M.Naghiyev (Baku, 2018), Materials of the XXVI International Scientific Conference of students, postgraduates and young scientists “Lomonosov-2019”, section “Chemistry” (Moscow, April 8-12, 2019), International conference “Achievements and perspectives of modern chemistry” dedicated to the 60th anniversary of the Institute of Chemistry (Chisinau, Republic of Moldova, October, 9-11, 2019), International Conference on “Actual problems of chemical engineering”, dedicated to the 100th anniversary of the Azerbaijan State Oil and Industry University (Baku, 24-25 December, 2020).

Name of the organization where the dissertation work is carried out. The dissertation work was carried out in the laboratory "Chemistry and technology of alkylphenols" in 2020-2021 according to the research work plan (17/2017) conducted in this direction at the Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev of the Azerbaijan National Academy of Sciences.

Personal presence of the author. The main ideas included in the dissertation, problem statement, directions of research and their implementation, experiments and tests, systematization and analysis of the obtained results, generalization of the main results of the dissertation were carried out with the personal participation of the author.

Volume and structure of the work. The dissertation consists of an introduction, 7 chapters, results, 345 used literature sources and appendices. The dissertation contains 30 tables, 30 figures, 26 graphs, 8 schemes and covers a total volume of 298 printed pages. The dissertation consists of 322704 characters, except for pictures, tables, bibliography and appendices (introduction 13560, Chapter I 93167, Chapter II 24473, Chapter III 60902, Chapter IV 47450, Chapter V 29613, Chapter VI 12759, Chapter VII 34578 and result

6202).

The introduction substantiates the relevance and degree of development of the topic, the object, subject, research goals and objectives, research methods, the main provisions of the defense, the scientific novelty of the dissertation, the theoretical and practical significance of the research, the approbation, structure and scope of the work, the essence of the chapters is briefly described.

The first chapter provides a review of the literature in accordance with the topic of the dissertation. The literature on alkyimidazoles and their production, aliphatic reactions with aliphatic and cyclic hydrocarbons obtained from the condensation of isoprene and piperilen with ethylene in the C₅-fraction obtained from the pyrolysis of low-octane gasoline with the presence of various catalysts, at the same time, the literature on the Mannix-based aminomethylation reactions of alkylphenols was analyzed. Also, this chapter covers a wide range of applications of chemical compounds modified with nitrogen-containing imidazolines. At the end of the literature review, a critical analysis of the existing research in the field presented is given and the scientific direction of the research work is substantiated.

The second chapter gives an experimental part. This section provides raw materials, their physical and chemical characteristics, the course of experiments and a description of the equipment used, methods of analysis of raw materials used for research and target products obtained as a result of the reaction.

The third chapter is devoted to the study of alkylation reactions with methylcyclohexanes obtained from gas processing processes in the presence of *para*-cresol catalyst KU-23, and **the fourth chapter** with zeolite-Y catalyst impregnated with orthophosphate acid. Here, the intermittent and uninterrupted *para*-cresol catalytic alkylation reactions with methylcyclohexanes in a pilot device are described.

The fifth chapter deals with the production of *para*-methylcyclohexyphenols and new (2-methylcyclohexyl)-4-methylphenols with aminoethylnonylimidazoline and Mannix bases, modified composites with alkyimidazoles.

The sixth chapter deals with the aminoethylnonylimidazole aminoethylmethylation of space-difficult cycloalkylphenols, the production of modification products with alkyylimidazole, and **the seventh chapter** on the use of methylcyclohexylphenols with aminoethylnonylimidazoline and Mannix bases.

As a summary of the completed scientific work, the dissertation concludes with the main results, a list of references and appendices.

MAIN CONTENT OF THE WORK

Primary raw materials, catalysts, experimental rules and methods of analysis of reaction products

Para-cresol, 1- and 3-methylcyclohexenes, 1-methyl-3-isopropenyl-cyclohexene-1-y (diprene), 1-methyl-4-isopropenyl-cyclohexene-1-year (dipentene), the mixture of isoprene cyclodimers (160-180°C fraction), formalin, aminoethylnonylimidazoline, polyethylpoliamine (PEPA), natural petroleum acid (NPA), alkyylimidazoline, oxyethylated *para*-nonylphenol, solvents - benzene, hexane, toluene, isooctane is used as raw materials for scientific research.

Para-cresol (*p*-cresol) has the following physico-chemical properties: boiling point - 202°C; melting point - 35°C; molecular weight 108.

1-Methylcyclohexane (1-MTCH) is obtained by condensation of isoprene with ethylene at 99.8% purity, and 3-methylcyclohexane (3-MTCH) at 98.6% purity by piperylene with ethylene.

1-MTCH has the following physicochemical properties: boiling point - 110-111°C, irradiance coefficient $n_D^{20} - 1.4500$, density, $g/cm^3 - 0.8200$, molecular weight - 96.

Physicochemical properties of 3-MTCH: boiling point - 103-104°C, irradiance coefficient $n_D^{20} - 1.4530$, density, $g/cm^3 - 0.8142$, molecular weight - 96.

Diprene (DP) is obtained from the reaction of cyclodimerization of isoprene in an autoclave and, after removal and

purification, has the following physicochemical properties: boiling point - 160-161°C, irradiance coefficient $n_D^{20} - 1.4656$, density, $g/cm^3 - 0.8347$, molecular weight - 136.

Dipentene (DPT) is obtained from the reaction of cyclodimerization of isoprene in an autoclave and, after removal and purification, has the following physicochemical properties: boiling point - 174-175°C, irradiance coefficient $n_D^{20} - 1.4745$, $\rho_4^{20} - 0.8476$, molecular weight - 136.

The isoprene cyclodimer (160-180°C fraction) (ICD) is obtained from the cyclodimerization of isoprene in an autoclave. 160-180°C fraction is expelled from the obtained product. ICD consists mainly of a mixture of DP and DPT and has the following physicochemical properties: Tg - 160-180°C, irradiance coefficient $n_D^{20} - 1.4735$, density, $g/cm^3 - 0.8458$, molecular weight - 136.

Formalin is an aqueous solution of formaldehyde (30%).

Aminoethylnonylimidazoline: empirical formula - $C_{14}H_{30}N_3$; average molecular weight - 240; irradiance coefficient $n_D^{20} - 0.9860$; density, $g/cm^3 - 0.1098$.

PEPA: average molecular weight - 230, boiling point - 206-288°C, $n_D^{20} - 1.5110$, density, $g/cm^3 - 0.1009$.

NPA: average molecular weight - 220, boiling point - 110-220°C, irradiance coefficient $n_D^{20} - 1.4772$, density, $g/cm^3 - 0.8840$.

Alkylimidazoles (taking NPA:PEPA 2:1 mol) - kinetic viscosity, mm^2/s , at 100°C - 243.31; amount of ash, % - 0.02; density 20°C, $g/cm^3 - 1.001$; freezing point, °C - 20.

Oxyethylated nonylphenol (ONP) (imported from the Russian Federation, ATSC "Nizhnekamskneftexim" of the Republic of Tatarstan (Nizhnekamsk) and corresponds to TU 2483-077-05766801-98) - kinematic viscosity, mm^2/s , at 100°C - 363.81; density ρ_4^{20} at 20°C, $g/cm^3 - 1.0630$; irradiance coefficient $n_D^{20} - 1.4903$.

KU-23 (GOST 20298-74) and zeolite-Y impregnated with orthophosphate acid were used for alkylation reactions.

The zeolite-Y catalyst impregnated with orthophosphate acid is prepared as follows: it is perfectly mixed with the alumogel cracking catalyst (Zeolite-Y, $\text{SiO}_2: \text{Al}_2\text{O}_3 = 4.8$, ion exchange rate 97%). The obtained mass is passed through a sieve with a diameter of 1.6 mm, granulated and incandescent. The catalyst is then impregnated with 10% orthophosphate acid (according to P_2O_5), evaporated, dried in an oven at 100°C , and heated by continuously raising the temperature from 200°C to 600°C . The catalyst is then cooled and used.

Alkylation reactions of *p*-cresol with cycloolefins in the laboratory were carried out in a three-necked flask by a known method.

Figure 1 shows the schematic diagram of the catalytic alkylation process of *p*-Cresol with a capacity of 2 kg/h in a pilot plant operating continuously with cycloolefins.

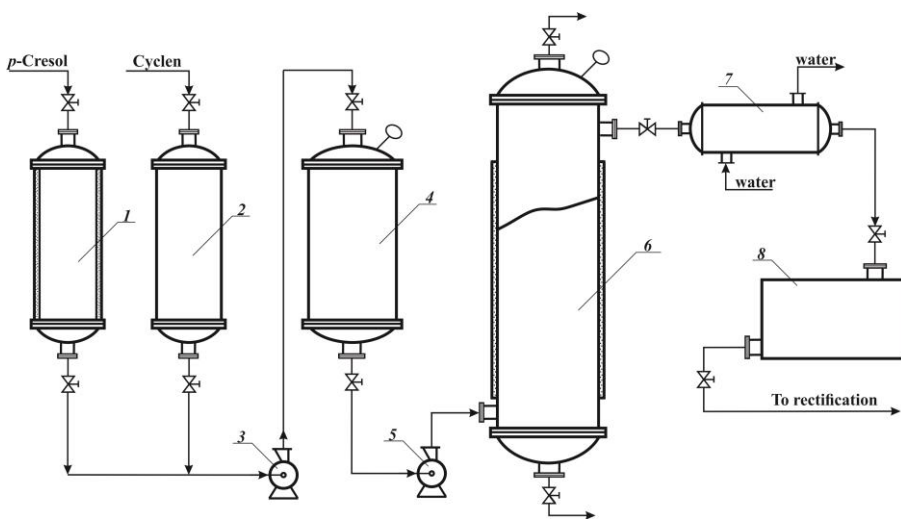


Figure 1. Principle technological scheme of catalytic cycloalkylation reactions of *p*-cresol with methylcyclohexanes:

1 - capacity for *p*-cresol; 2 - capacity for cyclone; 4 - mixer; 3, 5 – nasos; 6 - reactor; 7 - refrigerator; 8 - capacity for alkylate

p-Cresol (1) and cyclene (2) are fed to the mixer in the calculated ratio (4). In the capacity of *p*-cresol (1) the temperature is maintained at 40°C . A mixture of *p*-cresol and methylcyclohexane is

fed from the mixer to the lower part of the reactor (6). The mixture of components passes through the catalyst and is collected in the tank (8) after cooling in the refrigerator (7); sent to rectification from the alkylate (8) tank. In the rectification process, first unreacted cycloolefins are released, then *p*-cresol and target products are separated in a vacuum (10 mm Hg).

At the end of the experiment, the supply of raw materials is stopped, the product inside the reactor is discharged into the receiving tank and the reactor is switched to regeneration mode (after 500 hours of operation). Regeneration of the zeolite-Y catalyst impregnated with orthophosphate was carried out directly in the reactor.

Mannix-based reactions of obtained 2-cycloalkyl-4-methylphenols with formaldehyde and aminoethylnonylimidazoline were investigated in a three-throat flask. The calculated amount of 2-cycloalkyl-4-methylphenol, amine and solvent (benzene) is filled into the flask and heated. When the temperature reaches 25-30°C, 30% formalin is added to the flask in the calculated amount from the dropper funnel for 45 minutes. After the addition of formalin, the reaction temperature is raised to 80°C and the mixing is continued for another 1-2 hours.

Alkylimidazoles were obtained as follows: the calculated volume of NPA was filled into a three-necked flask and heated to 80°C. Then PEPA is added to it piece by piece. In this case, the process is continuously supplied with nitrogen to prevent the acquisition of by-products. After PEPA is added, the temperature is raised to 140°C and mixed for 3-3.5 hours. In this case, the separated water is removed from the process. The temperature of the reaction mixture is then raised to 220-240°C and stirred at this temperature for 2-2.5 hours. In this case, the separated water is removed from the process. Subsequent modifications of the obtained alkylimidazoles were obtained by mixing with cycloalkylphenols in different proportions.

Modifications of ONP with alkylimidazoles were obtained in a pilot plant installed at the Tural-110 research and production facility in Sumgayit (Figure 2).

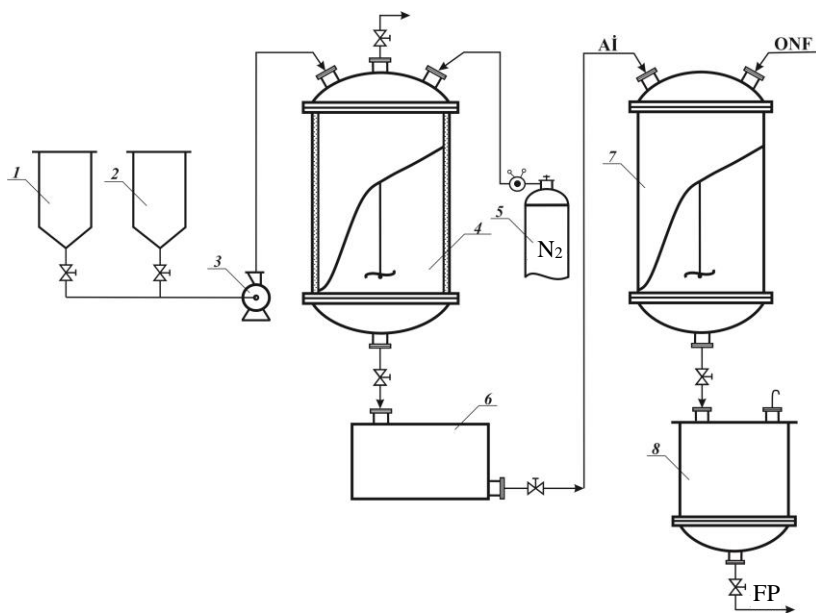


Figure 2. Scheme of the process of obtaining modifications of alkylimidazoles with cycloalkylphenols and ONP obtained from the interaction of NPA and PEPA in the nitrogen medium: 1- Capacity for NPA; 2- capacity for PEPA; 3- pump; 4- reactor; 5- nitrogen balloon; 6- capacity for imidazoline; 7- reactor; 8- capacity for the finished product (FP).

NPA (1) and PEPA (2) are fed to the reactor (4) by pumping in a 2:1 ratio (3) as shown earlier. The process is carried out as described above. At the end of the reaction, the nitrogen (5) supplied to the reactor (4) is stopped, the process is stopped and the product is sent to the tank (6). In the next step, the calculated amount of imidazoline (6) is transferred from the tank (7) to the reactor. A calculated amount of cycloalkylphenol (or ONP) is added to the reactor (7) at the same time. For the production of modifications of alkylimidazole and cycloalkylphenols were taken in 1:1 mass ratios. The mixture is stirred at 40°C for 1 hour, then emptied into a container while hot (8) and sent for use.

Fractovan-model 2150 «Carbon Erba» (Italy), LXM-72 and thin-layer chromatographic analysis methods were used to determine

the composition and purity of the synthesized products.

Density of synthesized products (ρ_4^{20}) was determined by ASTM D5002 method on AntonPaar device "DMA 4500M", radiation coefficient (n_D^{20}) was determined by refractometric method on AntonPaar device "Abbemat 500" method, and viscosity was determined by ASTM D445 method on AntonPaar device "Atabinger SVM".

Molecular weight was determined on a mass spectrometer MX-1303 at a temperature of 200°C, ionized voltage 70 eV, emulsion current 1 mA. The mass spectrum was also measured using Hewlett Paekord's GC/MS chromatom mass spectrometer.

The IR spectra of the obtained compounds were recorded on "Spectrum BX" spectrometers manufactured by "Perkin-Elmer" and "ALPHA IQ Fourier" (AFR) produced by BRUKER

The NMR spectrum of the obtained compounds was recorded on a 300 MHz NMR spectrometer (AFR) manufactured by "BRUKER".

The electrical conductivity of the synthesized products is determined using the Hungarian Conductivity TVPE:ok-102/1 conductometer.

A "STA PT 1600 LINSEIS" differential scanning calorimeter was used to measure the endo- and exothermic transition phases of the thermal analysis of the synthesized products as a function of temperature.

Some features of *p*-cresol alkylation reactions with methylcyclohexene and KU-23 catalyst

Cycloalkylation reactions of *p*-cresol with 1(3)-methylcyclohexanes and cyclodimers of isoprene in the presence of KU-23 catalyst were studied in a pilot plant operating intermittently and continuously.

Interactions of *p*-cresol with methylcyclohexanes in an intermittent device

Here, the kinetic factors (temperature, reaction time, mole ratios of the initial components, the amount of catalyst) affecting the

yield and selectivity of the products of the cycloalkylation reaction of *p*-cresol with methylcyclenes were studied. Under the optimal conditions found, the target products were found to have high yield and selectivity.

For example, the results of cycloalkylation reactions of *p*-cresol with 1-methylcyclohexene in the presence of KU-23 catalyst are given below.

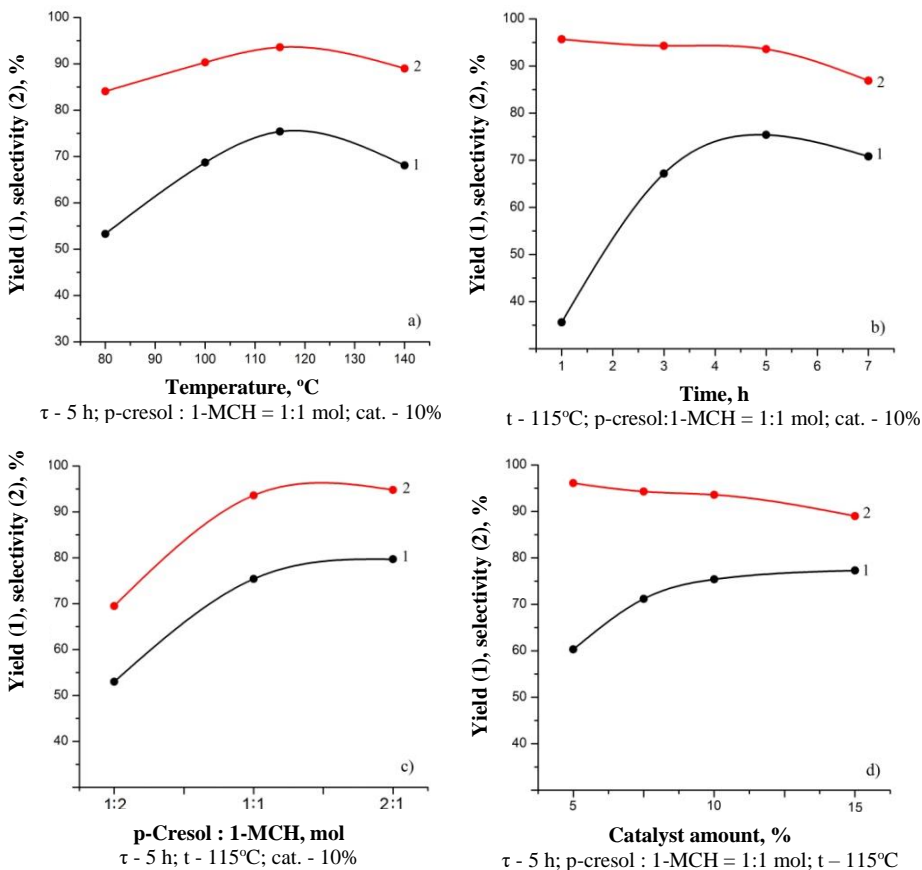
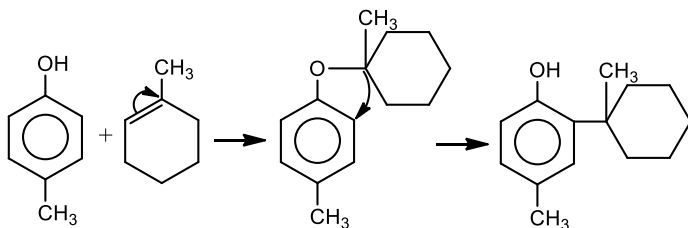


Figure 3. 2(1-Methylcyclohexyl)-4-methylphenol yield (1) and selectivity (2) dependence curves on temperature (a), time (b), mole ratios of initial components (c), catalyst amount (d)

Figure 3 shows the curves of the dependence of the yield and selectivity of 2(1-methylcyclohexyl)-4-methylphenol, obtained by the reaction of *p*-cresol with 1-methylcyclohexane, on the reaction temperature, molar ratios of the starting materials, and catalyst consumption.

The results of the research show that it is not expedient to take the temperature of the cycloalkylation reaction at 80, 100°C to carry out the interaction of *p*-cresol with 1-methylcyclohexane. At these temperatures, the yield of the target product is 53.3-69.7%, and the selectivity is 84.1-90.3% for the target product. The low selectivity of the target product at low temperatures is explained by the formation of methylcyclohexylphenyl ether as a result of the cycloalkylation reaction:

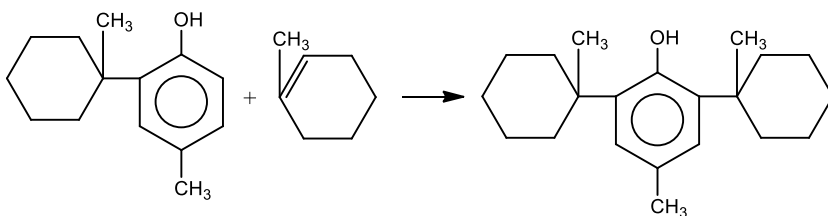


As the temperature of the cycloalkylation reaction increases, the methylcyclohexyl group migrates to the *ortho*-state of the aromatic ring (Claisen grouping). As a result, at a temperature of 115°C, the yield of the target substance is 75.4%, and the selectivity is 93.6%. At a further increase in the reaction temperature (at 140°C), the yield and selectivity of the target product are 68.1 and 89.0%, respectively.

It can be seen from Figure 3 that when the initial raw materials meet the catalyst for 1 and 3 hours, the consumption of the target products is 35.6 and 62.2%, and the selectivity is 95.7 and 94.3%. When the reaction time is 5 hours, the yield and selectivity of the target substance are 75.4 and 93.6%, respectively, which can be considered effective. By increasing the reaction time to 7 hours, the yield and selectivity of the target product change slightly.

As can be seen from Figure 3, the efficient yield and selectivity

of the target product is obtained at molar ratios of the primary raw materials at 1:1 moles. Increasing the concentration of 1-methylcyclohexane in the reaction mixture reduces the yield (53.0%) and selectivity (69.5%) of the target product. This reaction is explained by the reaction of the already taken cyclene with 2(1-methylcyclohexyl)-4-methylphenol to form 2,6-di-substituted *p*-cresol:



By doubling the amount of *p*-cresol in the mixture, the yield of the target substance is 79.7% and the selectivity is 94.8%. However, this time the yield and selectivity increase by 2-3%. But, it is not economically viable to double the amount of *p*-cresol due to a slight increase in the yield and selectivity.

By taking 5% of the catalyst consumption for the alkylation reaction, the yield of the target product is 60.3%. When the consumption of the catalyst is more than doubled (10%), the yield and selectivity of the target substance can be effectively assumed. By increasing the amount of catalyst by 15%, the yield increases to 77.3%, but the selectivity decreases to 89%.

As a result of the research, effective conditions were found for the cycloalkylation reaction of *p*-cresol with 1-methylcyclohexane in the presence of KU-23 catalyst: reaction temperature - 115°C, duration - 5 hours, molar ratios of initial components - 1:1, catalyst content - 10%. Under these conditions, the yield of the target product - 2(1-methylcyclohexyl)-4-methylphenol is 75.4% for the *p*-cresol, and the selectivity is 93.6% for the target product.

The IR and ¹H, ¹³C NMR spectra of 2(1-methylcyclohexyl)-4-methylphenol are given in Figure 4-6.

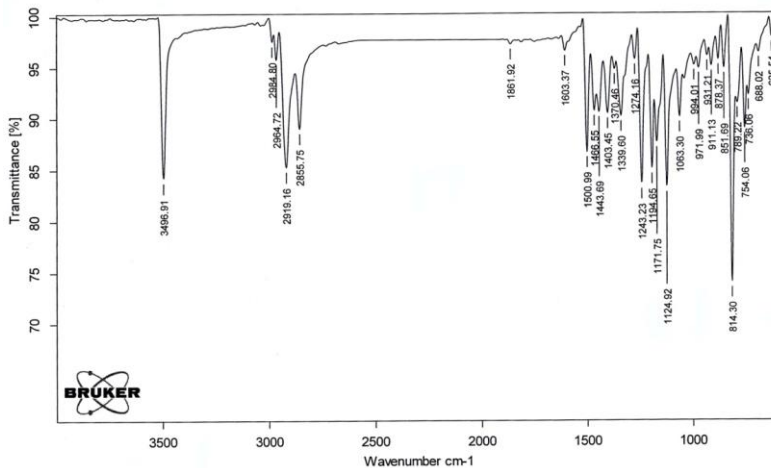


Figure 4. IR spectrum of 2(1-Methylcyclohexyl)-4-methylphenol

The following sliding bands were observed in the IR spectrum of 2(1-methylcyclohexyl)-4-methylphenol: 814, 878 cm^{-1} - 1,2,4-substituted benzene ring; 1063, 1124, 1171 cm^{-1} - deformation shift of O – H group in phenol; 1243, 1274 cm^{-1} - C – O bond in phenol; 3496 cm^{-1} - valence shift of O – H bond in OH group; 1500 cm^{-1} - benzene ring; 1603 cm^{-1} - C = C bond of benzene; 1339, 1370, 1403, 1443 cm^{-1} - deformation sliding of CH₃ and CH₂ groups; 2855, 2919, 2964, 2984 cm^{-1} - Valence shifts of CH₃ and CH₂ groups.

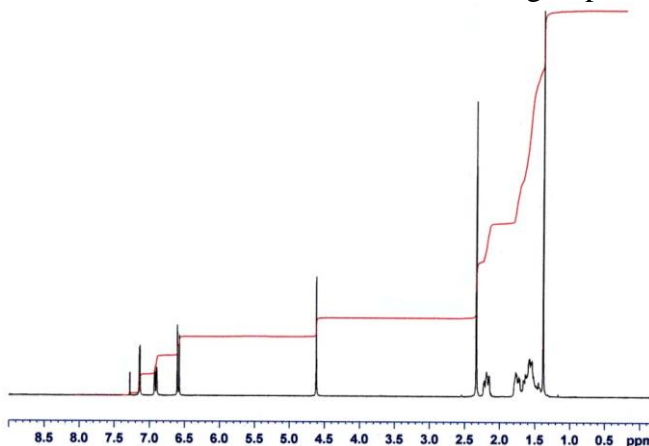


Figure 5. ¹H NMR spectrum of 2(1-Methylcyclohexyl)-4-methylphenol

Results of ^1H NMR spectroscopic study of 2(1-Methylcyclohexyl)-4-methylphenol (CDCl_3 , δ , ppm): 1.38 (singlet, 3H, CH_3); 1.54-2.22 (multiplet, 10H, 5 CH_2); 2.33 (singlet, 3H, CH_3); 4.61 (singlet, 1H, OH); 6.57-6.60 (d, 1H, arom.); 6.90-6.93 (d, 1H, arom.); 7.4 (singlet, 1H, arom.).

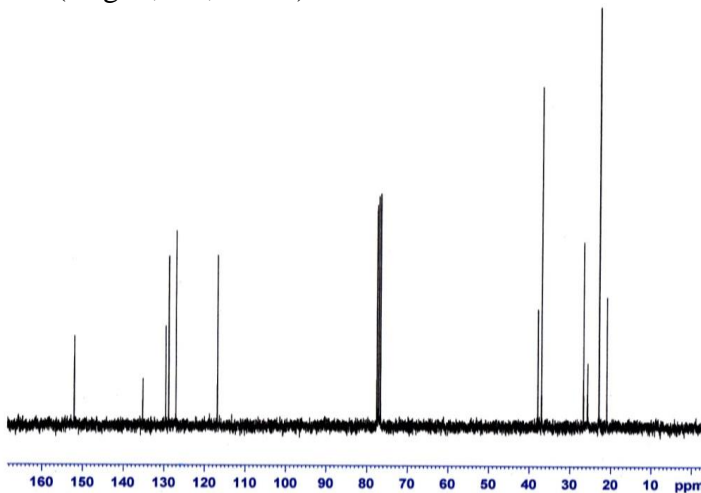


Figure 6. ^{13}C NMR spectrum of 2(1-Methylcyclohexyl)-4-methylphenol

^{13}C NMR spectrum results (CDCl_3 , δ , ppm): 20.9 (CH_2 , in a cycle); 22.8 (2CH_2 , cycle); 25.6 (CH_3 , cycle); 26.6 (CH_3 , arom. in the ring); 36.9 (2CH_2 , cycle); 37.8 (C, cycle); 116.8 (CH, arom.); 127.0 (CH, arom.); 128.8 (CH, arom.); 129.6 (C, arom.); 135.2 (C, arom.); 152.0 (C–O, arom.).

Thus, the chemical structure of 2(1-methylcyclohexyl)-4-methylphenol is fully confirmed.

A stepwise material balance for the production of 2(1-methylcyclohexyl)-4-methylphenol in the presence of a catalyst KU-23 has been compiled and the results are given below:

I. Cycloalkylation

Taken:	weight,g	%
1) <i>p</i> -Cresol	54.0	50.3
2) 1-Methylcyclohexene	48.0	44.7
3) KU-23	5.4	5.0
Total:	107.4	100.0

	Obtained:		
	– Alkylate + catalyst	106.7	99.3
	loss	0.7	0.7
		<hr/>	
	Total:	107.4	100.0
II.	Filtering		
	Taken:		
	– Alkylate + catalyst	106.7	100.0
		<hr/>	
	Total:	106.7	100.0
	Obtained:		
	– Alkylate	100.5	94.2
	– KU-23	5.2	4.9
	loss	1.0	0.9
		<hr/>	
	Total:	106.7	100.0
III.	Rectification		
	Taken:		
	– Alkylate	100.5	100.0
		<hr/>	
	Total:	100.5	100.0
	Obtained:		
	1) Returning 1-MTSH	7.6	7.6
	2) Returning <i>p</i> -cresol	9.8	9.7
	3) 2(1-MTSH)- <i>p</i> -cresol	76.9	76.5
	4) 2,6-di(1-MTSH)- <i>p</i> -cresol	3.4	3.4
	5) Residue	1.5	1.5
	loss	1.3	1.3
		<hr/>	
	Total:	100.5	100.0

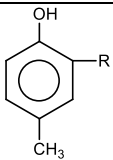
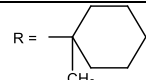
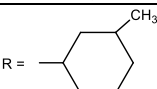
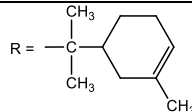
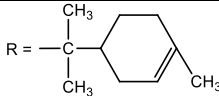
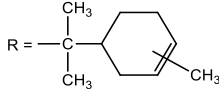
From the balance of the presented material it is shown that taking the amount of *p*-cresol 54.0 g (0.5 mol), the amount of 1-methylcyclohexene 48.0 g (0.5 mol), 76.9 g 2(1-methylcyclohexyl)-4-methylphenol is obtained, which is 75.4% of the yield. (according to the *p*-cresol taken). Under these conditions, 3.4 g of 2,6-disubstituted *p*-cresol and 1.5 g of resin-like substance are obtained as by-products, which reduces the selectivity to 96.3%.

Interactions of *p*-cresol with 3-methylcyclohexene and isoprene cyclodimers using KU-23 catalyst were also investigated.

Physico-chemical parameters of synthesized 2(methylcyclohexyl)-4-methylphenols are given in Table 1.

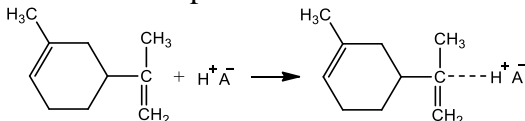
Table 1

**Physico - chemical properties of 2(methylcyclohexyl)-
4-methylphenols**

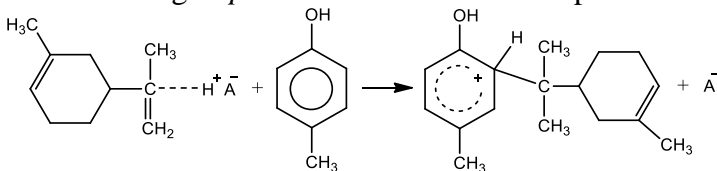
	T _{boil.} , °C (10 mm Hg)	T _{melt.} , °C	n _D ²⁰	ρ ₄ ⁴⁰	Mol. mass	Element composition, %	
						<u>Calculated</u>	
						<u>Found</u>	
						C	H
	167-170	45	–	–	204	<u>82.4</u> 82.0	<u>9.8</u> 9.6
	161-163	41	–	–	204	<u>82.4</u> 81.8	<u>9.8</u> 9.4
	202-205	–	1.5035	1.0133	244	<u>83.6</u> 83.3	<u>9.8</u> 9.5
	212-215	–	1.5267	1.0375	244	<u>83.6</u> 83.2	<u>9.8</u> 9.4
	204-215	–	1.5133	1.0284	244	<u>83.6</u> 83.4	<u>9.8</u> 9.3

The probable mechanism of *p*-cresol alkylation reactions with methylcyclohexanes is considered in the example of *p*-cresol alkylation reaction with diprene.

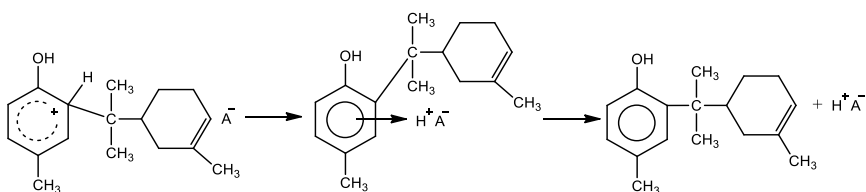
Initially, the interaction of the catalyst with diprene forms a catalyst-cyclic polarization complex:



The polarization complex is then converted to carbocation, which acts on the benzene ring of *p*-cresol to form the π -complex:



During the conversion of the π -complex to the δ -complex, a covalent bond is formed between the isopropylcyclohexenyl and the carbon atom of the aromatic ring. In this case, since the electronic action of the hydroxyl group is captured by the parachide CH_3 atom, it forms an δ -complex with the carbon atom in the orthostatic state. The resulting δ -complex is not stable and is easily converted to the π -complex; it is converted to a stable 2(3-methylcyclohexene-3-yl-isopropyl)-4-methylphenol by donating a proton:



The diprene has two double connections, one in the side chain and the other in the cycle. The double bond of cyclohexene is more stable than the double bond of the isoprenyl radical in the side chain. Therefore, the catalyst primarily carbates with the isopropenyl radical of diprene. More severe conditions are required for diprene to react with cyclohexenyl radicals.

Alkylation reactions of *p*-cresol with methylcyclohexene in a continuous pilot plant

Catalytic alkylation reactions of *p*-cresol with 1- and 3-methylcyclohexenes and isoprene cyclodimers were also performed in a continuous pilot plant. The purpose of conducting the *p*-cresol alkylation process in a continuously operating pilot plant is to lay the groundwork for the results of our research to be carried out on an industrial scale in the future on an industrial plant. Carrying out the process on a continuous pilot plant reduces the cost of the product and simplifies the technology of the process. For this reason, we decided to study the cycloalkylation reactions of *p*-cresol with methylcyclohexene in a continuously operating pilot plant.

For example, the results of cycloalkylation reactions in a pilot plant operating continuously with 1-methylcyclohexane in the

presence of *p*-cresol catalyst KU-23 are given.

In order to achieve high yield and selectivity of 2(1-methylcyclohexyl)-4-methylphenol, the effect of reaction temperature, molar ratios of initial components and volume rate on the direction of cycloalkylation reaction was studied. To find the effective yield and selectivity of 2(1-methylcyclohexyl)-4-methylphenol, the reaction temperature was 80-140°C, the molar ratio of *p*-cresol to 1-methylcyclohexene was 1:2 to 2:1, the volume rate was 0.2-1.0 h⁻¹.

Figure 7 shows the results of cycloalkylation reactions with 1-methylcyclohexane in a continuously operating pilot plant in the presence of *p*-cresol catalyst KU-23.

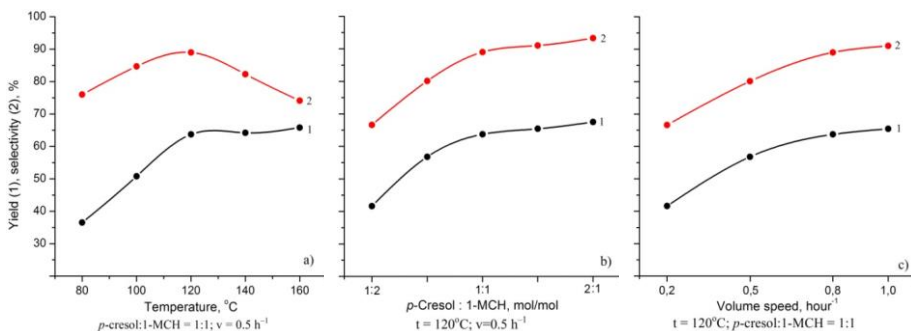


Figure 7. Dependence curves of the yield (1) and selectivity (2) of 2(1-methylcyclohexyl)-4-methylphenol from temperature (a), mole ratios of para-cresol to 1-MTSH (b) and volume velocity (c)

Figure 7 shows that for the cycloalkylation reaction of *p*-cresol with 1-methylcyclohexane, the yield of the target product obtained at temperatures of 80, 100°C is 36.5-50.8%, and the selectivity is 76.0-84.7% for the target product. The low yield of the reaction product indicates that the kinetic energies of the raw materials in the component mixture are not sufficient for the reaction to proceed to completion. The low selectivity for the target product is explained by the production of cyclohexyphenyl ether at low temperatures.

When the temperature of the cycloalkylation reaction is increased to 120°C, the yield of the target product increases to 63.7% and the selectivity to 89.0%. Subsequent increases in the temperature

of cycloalkylation reactions increase the yield of the target product to 65.8%, but the selectivity decreases to 74.1%. This reaction is explained by the addition of undesirable substances in the products of cycloalkylation with increasing temperature.

Figure 7 shows that when the amount of 1-methylcyclohexene in the mixture of primary raw materials taken for the reaction is doubled, the yield of the target product is 41.6% (for *p*-cresol) and the selectivity is 66.6% for the target product. The low yield and selectivity of the reaction product is explained by the increase in the amount of 2,6-di-substituted methylcyclohexyl-4-methylphenol in the final product during the overdose of 1-methylcyclohexene. The figure shows that a 1:1 ratio of *p*-cresol to 1-methylcyclohexene in moles provides high yield and selectivity of the target product. In this case, the yield of 2(1-methylcyclohexyl)-4-methylphenol is 63.7%, and the selectivity is 89.0%. By doubling the concentration of *p*-cresol in the mixture of components taken, the yield and selectivity of the target product are increased to 67.5% and 93.3%, respectively, which is not economically and technologically viable.

Figure 7 shows that at a rate of 0.5 h^{-1} volume of the mixture of components, it is possible to achieve efficient yield and selectivity of the target product.

Analysis of the experimental results shows that the effective conditions for cycloalkylation reactions with 1-methylcyclohexane in a continuously operating pilot plant in the presence of *p*-cresol catalyst KU-23 are as follows: temperature - 120°C , molar ratio of *p*-cresol to 1-methylcyclohexene - 1:1, volume rate - 0.5 h^{-1} . Under these conditions, the yield of 2(1-methylcyclohexyl)-4-methylphenol for *p*-cresol is 63.7%, and the selectivity is 89.0% for the target product.

The IR and ^1H , ^{13}C NMR spectra of 2(1-methylcyclohexyl)-4-methylphenol coincide with the results of the previously given spectra.

The final material balance for the production of 2(1-methylcyclohexyl)-4-methylphenol in a continuously operating pilot plant in the presence of KU-23 catalyst has been compiled and the results are given below:

I. Cycloalkylation			
Taken:		weight, g	%
1) <i>p</i> -Cresol		54.0	52.9
2) 1- Methylcyclohexene		48.0	47.1
		<hr/>	
		Total:	102.0 100.0
Obtained:			
– Alkylate		100.8	98.8
loss		1.2	1.2
		<hr/>	
		Total:	102.0 100.0
II. Rectification			
Taken:			
– Alkylate		100.8	100.0
		<hr/>	
		Total:	100.8 100.0
Obtained:			
1) Returning 1-methylcyclohexane		11.5	11.4
2) Returning <i>p</i> -cresol		14.7	14.6
3) 2 (1-methylcyclohexyl) - <i>p</i> -cresol		65.0	64.5
4) 2,6-di-(1-methylcyclohexyl)- <i>p</i> -cresol		5.8	5.7
5) Residue		2.2	2.2
loss		1.6	1.6
		<hr/>	
		Total:	100.8 100.0

It can be seen from the material balance of the process that 65.0 g of target product, 5.8 g of 2,6-di-substituted *p*-cresol, 2.2 g of resin-like residue were obtained from the rectification of alkylate obtained from alkylation reaction, which shows that the yield of target product is 63.7% and selectivity is 89.0%.

At the same time, cycloalkylation reactions of *p*-cresol with 3-methylcyclohexene and cyclodimers of isoprene were studied in a pilot device operating continuously in the presence of KU-23 catalyst, the effect of various parameters on the yield and selectivity of the target product was studied.

Study of alkylation reactions of *p*-cresol with methylcyclohexene in the presence of zeolite-Y catalyst impregnated with orthophosphate acid

Interaction reactions of *p*-cresol with 1- and 3-methylcyclohexene and cyclodimers of isoprene in the presence of orthophosphate acid-impregnated zeolite-Y catalyst were studied.

In order to obtain high yields and selectivity of the target products - 2(methylcyclohexyl)-4-methylphenols in the intermittent device, the effect of temperature, time, molar ratios of raw materials and catalyst consumption on the composition of the reaction products was studied. Temperature for cycloalkylation reactions was 70-130°C, time 2-6 hours, mole ratio of *p*-cresol to methylcyclohexene 1:2 ÷ 2:1, catalyst consumption (for *p*-cresol taken) was studied in the range of 5-15%.

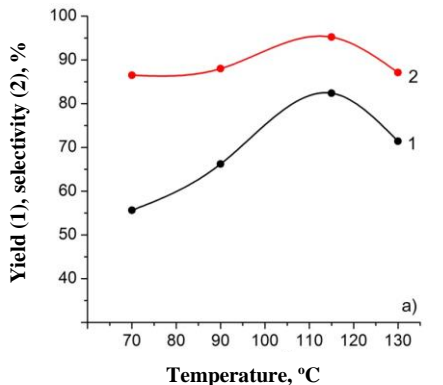
For example, let us examine the results of the interaction of *p*-cresol with 1-methylcyclohexane in the presence of a zeolite-Y catalyst impregnated with orthophosphate acid.

The results of the cycloalkylation reactions of *p*-cresol with 1-methylcyclohexane are given in Figure 8. The reaction temperature was 70-130°C, the time was 2-6 hours, the molar ratio of *p*-cresol to 1-methylcyclohexane was 1:2 to 2:1, and the amount of catalyst was studied at 5-15%.

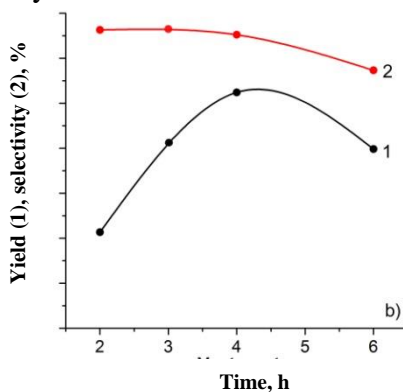
Figure 8 shows that when the reaction temperature is increased from 70 to 115°C, the yield of the target product increases from 55.6 to 82.4%. Selectivity for the target product is 95.7% at 115°C. By raising the reaction temperature to 130°C, the selectivity decreases to 87.1%. This is explained by the increase in the amount of di-substituted *p*-cresol in the alkylate with increasing temperature.

One of the main factors affecting the reaction is the contact time of the primary raw materials with the catalyst. It can be seen from Figure 8 that it is not possible to achieve an efficient yield of the target product within 2 hours of the reaction. In this case, the yield of the main product is 51.3% of the *p*-cresol taken. When the reaction time is 4 hours, the yield of the target product - 2(1-methylcyclohexyl)-4-methylphenol is 82.4%. It is not possible to achieve high results with increasing reaction time, as the yield

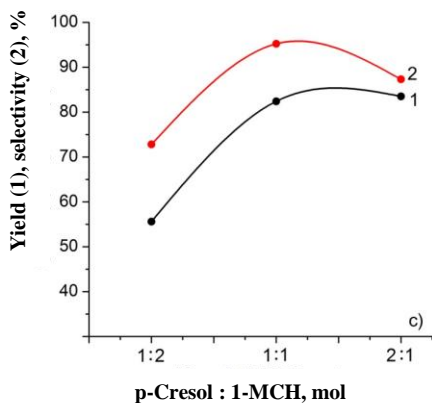
decreases to 69.8% and the selectivity to 87.3%.



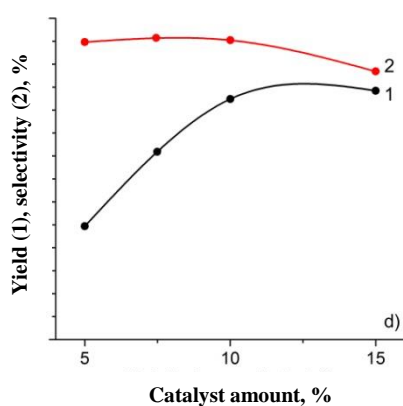
τ - 4 h; *p*-cresol : 1-MCH = 1:1 mol; cat. - 10%



t - 115°C; *p*-cresol:1-MCH = 1:1 mol; cat. - 10%



τ - 4 h; t - 115°C; cat. - 10%



t - 115°C, τ - 5 h; *p*-cresol : 1-MCH = 1:1 mol

Figure 8. Dependence curves of the yield (1) and selectivity (2) of 2 (1-methylcyclohexyl)-4-methylphenol from reaction temperature (a), time (b), molar ratio of primary raw materials (c) and catalyst amount (d)

One of the important factors influencing the yield and selectivity of 2(1-methylcyclohexyl)-4-methylphenol is the amount of raw materials taken for the reaction. Figure 8 shows that it is advisable to take the concentration of *p*-cresol and 1-methylcyclohexene in the raw material mixture to 1:1.

Figure 8 shows that by increasing the consumption of the catalyst taken for the alkylation reaction from 5 to 10%, the yield of the main product varies between 54.7-82.4%. When the consumption

of the catalyst used is 15%, the yield increases to 84.2%; however, in this case, the selectivity for the target product falls to 88.4%.

Analysis of the results of the experiments shows that the cycloalkylation reaction of *p*-cresol with 1-methylcyclohexane using the zeolite-Y catalyst impregnated with orthophosphate acid is recommended under the following conditions: temperature - 115°C, reaction time - 4 hours, mole ratio of *p*-cresol to 1-methylcyclohexene - 1:1, catalyst consumption for *p*-cresol - 10%. Under these conditions, the yield of 2(1-methylcyclohexyl)-4-methylphenol for *p*-cresol is 82.4%, and the selectivity for the main product is 95.7%.

IR, ¹H and ¹³C NMR spectra of 2(1-methylcyclohexyl)-4-methylphenol and their interpretation are given in the previous section.

Some properties of *p*-cresol catalytic alkylation reactions with methylcyclohexene in a continuous pilot device

Cycloalkylation reactions with 1- and 3-methylcyclohexenes and isoprene cyclodimers in the presence of *p*-cresol orthophosphate acid-impregnated zeolite-Y catalyst were also investigated in a continuous pilot plant.

For example, consider the results of cycloalkylation reactions of *p*-cresol with 1-methylcyclohexane.

In order to obtain high yield and selectivity of 2(1-methylcyclohexyl)-4-methylphenol, the effect of temperature, molar ratios and volume of raw materials on the composition of products obtained by cycloalkylation reaction was studied. The reaction temperature to obtain high yield and selectivity of 2(1-methylcyclohexyl)-4-methylphenol is 80-140°C, the molar ratio of *p*-cresol to 1-methylcyclohexene is 1:2 to 2:1, the volume rate is 0.2-1.0 h⁻¹.

Figure 9 shows the results of cycloalkylation reactions of *p*-cresol in the presence of a zeolite-Y catalyst impregnated with 1-methylcyclohexene and orthophosphate acid in a continuously operating pilot plant.

The figure shows that the catalytic cycloalkylation reaction of

p-cresol with 1-methylcyclohexane at a temperature of 120°C gives a yield of 67.3% (for *p*-cresol) and a selectivity of 96.1% for the target product. Taking the temperature of the cycloalkylation reaction to 80, 100°C, the yield and selectivity of the target product are in the range of 47.8-56.5% and 82.3-87.2%, respectively. The low yield and selectivity are explained by the production of cycloalkylphenyl esters at low temperatures. Raising the temperature of the cycloalkylation reaction above 120°C does not give such a high result.

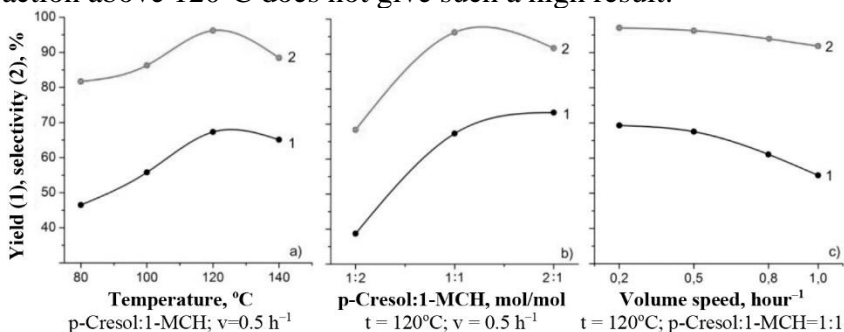


Figure 9. Dependence curves of the yield (1) and selectivity (2) of 2(1-methylcyclohexyl)-4-methylphenol from temperature (a), the mole ratio of *p*-cresol to 1-MTSH (b) and volume velocity (c)

Figure 9 shows that in order to obtain the effective yield of 2(1-methylcyclohexyl)-4-methylphenol - 67.3% and the selectivity - 96.1%, it is expedient to take *p*-cresol in a ratio of 1:1 mole to 1-methylcyclohexane. It is not possible to achieve such a high result by increasing or decreasing one or the other component in the mixture of raw materials supplied to the reactor. It can be seen from the figure that the yield and selectivity of the target product can be considered efficient at a rate of 0.5 h⁻¹ of the volume rate of the initial raw material mixture.

The analysis of the obtained experiments showed that in order to obtain high yield and selectivity during the cycloalkylation reaction of *p*-cresol with 1-methylcyclohexene in the presence of a zeolite-Y catalyst impregnated with orthophosphate, the reaction conditions should be taken as follows: reaction temperature - 120°C, molar ratio of *p*-cresol to 1-methylcyclohexene - 1:1, volume rate - 0.5 h⁻¹. Under these conditions, the yield of 2(1-methylcyclohexyl)-

4-methylphenol for *p*-cresol is 67.3%, and the selectivity is 96.1% for the target product.

The IR and ¹H, ¹³C NMR spectra of 2(1-methylcyclohexyl)-4-methylphenol overlap with the previously given spectra.

Final material balance for the production of 2(1-methylcyclohexyl)-4-methylphenol in a continuously operating pilot plant in the presence of a zeolite-Y catalyst soaked in orthophosphate acid compiled and the results are given below:

I. Cycloalkylation

Taken:	weight,g	%
1) <i>p</i> -Cresol	54.0	52.9
2) 1- Methylcyclohexene	48.0	47.1
<hr/>		
Total:	102.0	100.0
Obtained:		
– Alkylate	99.4	97.5
loss	2.6	2.5
<hr/>		
Total:	102.0	100.0

II. Rectification

Taken:		
– Alkylate	99.4	100.0
<hr/>		
Total:	99.4	100.0
Obtained:		
1) Returning 1-methylcyclohexene	12.6	12.7
2) Returning <i>p</i> -cresol	13.8	13.9
3) 2(1-methylcyclohexyl) - <i>p</i> -cresol	68.6	69.0
4) 2,6-di-(1-methylcyclohexyl)- <i>p</i> -cresol	1.7	1.7
5) Residue	1.1	1.1
loss	1.6	1.6
<hr/>		
Total	99.4	100.0

It can be seen from the material balance of the process that 68.6 g of target product, 1.7 g of 2,6-di-substituted *p*-cresol, 1.1 g of resin-like residue were obtained from rectification of alkylate obtained from alkylation reaction, which shows 67.3% of target product yield and 96.1% selectivity.

Similarly, cycloalkylation reactions of *p*-cresol with orthophosphate acid-impregnated zeolite-Y catalyst in a continuously

operating pilot plant with 3-methylcyclohexene and isoprene cyclodimers were studied, and the effect of various factors on the yield and selectivity of target products was studied.

The results of our research show that the cycloalkylation reactions with methylcyclohexenes in the presence of KU-23 and phosphate-impregnated zeolite-Y catalysts *p*-cresol, provided by us, take place in mild conditions and with high yield, unlike known catalysts. Table 2 shows the comparative results of cycloalkylation reactions of *p*-cresol with 1-methylcyclohexene using different catalysts.

Table 2

Comparative results of cycloalkylation reactions of *p*-cresol with 1-methylcyclohexene in the presence of known and proposed catalysts

Indicators \ Catalysts	NaHSO ₄ (known)	KU-2 (known)	KU-23	Zeolite-Y impreg- nated with ortho- phosphate acid
Temperature, °C	120	125	115	115
Time, hours	4.5	6	5	4
<i>p</i> -Cresol : 1-MTSH, mol/mol	2:1	1:1	1:1	1:1
The amount of catalyst, %	15	12	10	10
Composition of cycloalkylation products, % mass				
Cycloalkylphenyl ether	2.3	3.3	1.2	–
2-Monocycloalkyl <i>p</i> -cresol	92.1	89.2	93.1	95.3
2,6-di- cycloalkyl <i>p</i> -cresol	3.7	4.9	4.3	3.5
Residue	1.9	2.6	1.4	1.2
Yield, %	68.3	70.8	75.4	82.4
Selectivity, %	91.2	88.4	93.6	95.7

It can be seen from Table 2 that the cycloalkylation reactions in the presence of the proposed KU-23 and orthophosphate acid-impregnated zeolite-Y catalyst of *p*-cresol have more efficient kinetic parameters. In the presence of known catalysts, the yield of the target product - 2(1-methylcyclohexyl)-4-methylphenol is 68.3-70.8%, the selectivity is 88.4-91.2%, the yield of the proposed product is 78.6-82.4%, and the selectivity is 92.3-95.7%.

Figure 10 shows a diagram of the catalytic alkylation reactions of *p*-cresol with 1(3)-methylcyclohexanes and isoprene cyclodimers.

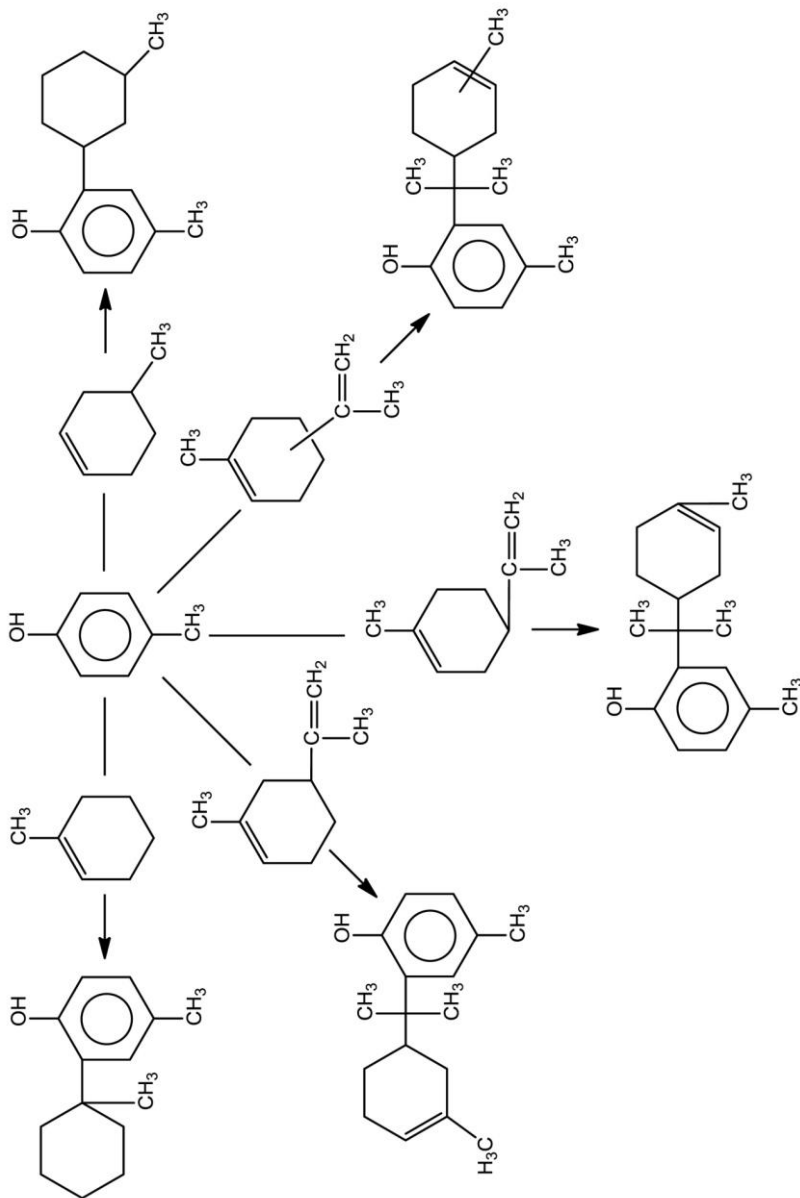


Figure 10. Scheme of alkylation reactions of *p*-cresol with methylcyclohexene in the presence of zeolite-*Y* catalysts impregnated with KU-23 and orthophosphoric acid

Compilation of a mathematical model of regression of the alkylation reaction of isoprene with cyclodimer in the presence of *p*-cresol catalyst KU-23 and solution of the optimization task

Based on the experimental data using the planning method of our experiments, a multidimensional regression model of the interaction of *para*-cresol with the cyclodimer of isoprene was developed. The dependence of the yield and selectivity of the target product on the amount of catalyst, time, temperature and the ratio of *para*-cresol to isoprene cyclodimer was studied. The relevance of the results obtained through the experiment was determined. The method of multifactorial orthogonal planning of the experiment, which consists of the study of all factors, was used to develop a regression model. Here, the input parameters of the optimization are indicated by X, and the output parameters by Y. Yield of the target product Y₁ and process selectivity Y₂ are the optimization factors. The rate of change of input parameters (X₁ - temperature; °C, X₂ - time, hour; X₃ - mole ratio of *para*-cresol with cyclodimers of isoprene, mol/mol; X₄ - amount of catalyst, %) is taken as follows:

$$80 \leq X_1 \leq 140; \quad 2 \leq X_2 \leq 7; \quad 1:2 \leq X_3 \leq 2:1; \quad 5 \leq X_4 \leq 15.$$

Statistical analysis was performed in the following stages: calculation of paired correlation coefficients; finding the coefficients of the regression equation; checking regression coefficients according to the Student's criterion; evaluation of the adequacy of the model using the Fisher criterion; calculation of errors of experimental indicators; estimation of variance.

The results of the calculations show that the correlation coefficients found are in the range of 0.3-0.8 on the Cheddock scale. $\text{corr}(1,2)=0.624$; $\text{corr}(2,3)=0.005$; $\text{corr}(3,4)=0.019$; $\text{corr}(5,6)=0.028$; $\text{corr}(4,5)=0.019$; $\text{corr}(1,3)=0.036$; $\text{corr}(1,4)=0.8$; $\text{corr}(1,5)=0.05$; $\text{corr}(2,4)=0.00481$; $\text{corr}(2,5)=0.008$; $\text{corr}(3,5)=0.032$.

It is clear from the results of the calculation that a strong correlation occurs between the first and second output variables, the first and fourth output variables. The correlation between other variables is weak.

To solve the optimization task, MatLab program, which keeps the modern algorithm in the linear programming task, was used. The maximum functionality is taken as the optimization limit:

$$F_{\max} = f(X_1, X_2, X_3, X_4, X_5)$$

the indicators of the process are taken as follows:

$$47 \leq X_1 \leq 47; \quad 24 \leq X_2 \leq 96; \quad 80 \leq X_3 \leq 140; \\ 2 \leq X_4 \leq 7; \quad 5 \leq X_5 \leq 15.$$

The solution of the optimization problem showed that the highest yield value $Y_{1\max}=74.42\%$ is within the following limits:

$$X_1 = 47; X_2 = 48; X_3 = 120.48; X_4 = 4.98; X_5 = 7.28;$$

$Y_{2\max}=94.86\%$ the price is within the following limits:

$$X_1 = 47; X_2 = 48; X_3 = 120.48; X_4 = 4.98; X_5 = 7.28$$

The results obtained by computer calculations are consistent with the experimental data (Table 3).

Table 3

Comparison of experimental and calculated indicators

The yield of the target product, %		Selectivity of the process, %	
Experimental	Calculated	Experimental	Calculated
45.4	46.34	88.2	87.68
60.7	61.28	90.8	90.37
76.5	74.42	95.3	94.86
64.9	65.37	89.4	89.13
74.3	72.63	86.1	86.64
70.6	68.86	89.7	89.37
61.2	59.15	83.6	83.08
54.7	55.68	87.3	85.97
73.3	72.11	91.4	90.73
75.5	74.27	93.6	92.18
64.6	64.53	92.0	92.67
70.1	68.95	93.2	93.59
75.8	72.21	96.3	94.24
77.9	76.57	94.7	93.75

Obtaining Mannix bases of 2(methylcyclohexyl)-4-methylphenols with aminoethylnonylimidazoline and modifications with alkylimidazoles

This section discusses the production of new composites from

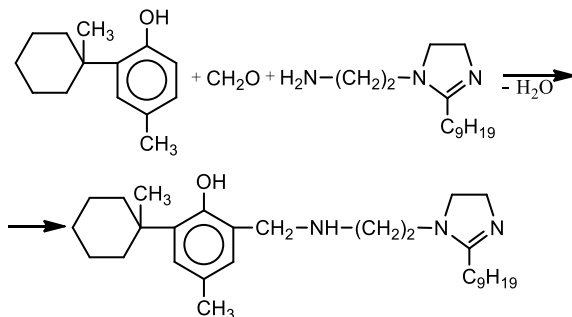
the modification of Mannix bases with alkylimidazoles by involving in the aminomethylation reactions of 2(methylcyclohexyl)-4-methylphenols with aminoethylnonylimidazole synthesized in various catalytic systems above.

Mannix bases of 2(methylcyclohexyl)-4-methylphenols

Methylcyclohexylimidazoles are obtained by the interaction of 2(methylcyclohexyl)-4-methylphenols with formaldehyde and amine in a 1:1:1 ratio.

For example, the synthesis of 2-hydroxy-3(1-methylcyclohexyl)-5-methylbenzylaminoethylnonylimidazole from the interaction of 2(1-methylcyclohexyl)-4-methylphenol with formaldehyde and aminoethylnonylimidazole is studied.

The aminomethylation reaction follows the following equation:



Fill a three-necked flask with 51.0 g of 2(1-methylcyclohexyl)-4-methylphenol, 60.0 g of aminoethylnonylimidazole, 51.0 g of benzene and heat by stirring. When the temperature reaches 40°C, 25.0 g of formalin is added. The experiment is then carried out in the method described above. The result is 90.4 g of 2-hydroxy-3(1-methylcyclohexyl)-5-methylbenzylaminoethylnonylimidazole, which represents a yield of 79.3%.

The following signals are observed in the ¹H NMR spectrum of synthesized 2-hydroxy-3(1-methylcyclohexyl)-5-methylbenzylaminoethylnonylimidazole: The cyclic structure of the substance is in the band $\delta = 1.35-1.6$ ppm, the signal of the CH₃ group is $\delta = 0.9-1.1$ ppm, the protons of the aromatic nucleus are $\delta = 6.75$ ppm, the

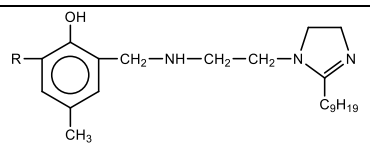



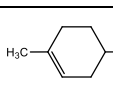
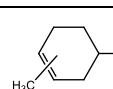
proton of the hydroxyl group attached to the aromatic nucleus is in the band $\delta = 6.5$ ppm, the intensity of the cyclohexene ring = 5.2-5.4 ppm in multiplet form, NH-group proton $\delta = 3.60$ ppm resonance signal, $-\text{CH}_2-$ radical proton $\delta = 4.70$ ppm bands were observed.

The following groups were found in the IR spectrum of 2-hydroxy-3(1-methylcyclohexyl)-5-methylbenzylaminoethylonylimidazole: OH group in the $3100-3500\text{ cm}^{-1}$ band, 1380 cm^{-1} - CH_3 group, C=C bond of the aromatic ring 1630 cm^{-1} , naphthenic ring slippage is observed in the 830 and 880 cm^{-1} bands. Para-replacement of benzene ring $828, 1240, 1590, 1610$ and 390 cm^{-1} ; NH-group 3050 cm^{-1} ; C-N was found in $1094, 1100, 1120, 1300\text{ cm}^{-1}$ strips.

Physico - chemical properties of 2-hydroxy-3(1-methylcyclohexyl)-5-methylbenzylaminoethylonylimidazole and other imidazolines are given in Table 4.

Table 4

Physico - chemical properties of 2-hydroxy-3(methylcyclohexyl)-5-methylbenzylaminoethylonylimidazole

	T _{boil} , °C (10 mm Hg)	n _D ²⁰	ρ_4^{40}	M.k.	Found, %		
					Calculated, %		
					C	H	N
 C ₂₉ H ₅₀ N ₃ O	218-226	1.6534	1.130	456	$\frac{76.3}{75.8}$	$\frac{11.0}{10.3}$	$\frac{9.2}{8.8}$
 C ₂₉ H ₅₀ N ₃ O	214-223	1.5903	1.116	456	$\frac{76.3}{75.6}$	$\frac{11.0}{10.4}$	$\frac{9.2}{8.7}$
 C ₃₂ H ₅₄ N ₃ O	230-234	1.6571	1.1445	496	$\frac{77.4}{77.0}$	$\frac{10.9}{10.5}$	$\frac{8.5}{8.0}$
 C ₃₂ H ₅₄ N ₃ O	236-240	1.6632	1.1577	496	$\frac{77.4}{76.8}$	$\frac{10.9}{10.6}$	$\frac{8.5}{7.8}$
 C ₃₂ H ₅₄ N ₃ O	230-240	1.6590	1.1530	496	$\frac{77.4}{76.9}$	$\frac{10.9}{10.4}$	$\frac{8.5}{7.7}$

Obtaining modifications of alkyimidazoles with 2(methylcyclohexyl)-4-methylphenols

In this section, modifications of the previously synthesized 2(methylcycloalkyl)-4-methylphenols with alkyimidazolines in the ratios of 2:1, 1:1 and 1:2 have been prepared and it was tested as a conservation by adding 5-10% to T-30 distillate oil as an antioxidant.

The composition of the prepared samples is given below:

1. T-30 o.d. + 2(1- methylcyclohexyl)-4- methylphenol + AIM
2. T-30 o.d. + 2(3- methylcyclohexyl)-4- methylphenol + AIM
3. T-30 o.d. + 2(3- methylcyclohexene -3-y- isopropyl)-4- methylphenol + AIM
4. T-30 o.d. + 2(4- methylcyclohexene -3-y- isopropyl)-4- methylphenol + AIM
5. T-30 o.d. + 2[3(4)- methylcyclohexene -3-y- isopropyl]-4- methyl-phenol + AIM

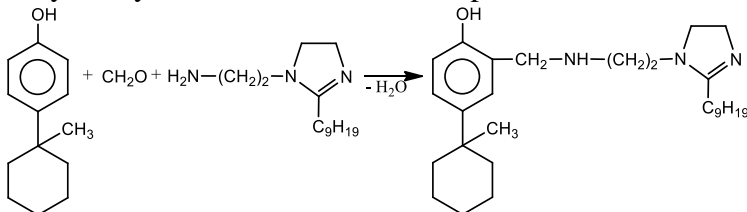
Physico - chemical parameters of the prepared compositions were determined.

Obtaining Mannix bases and modifications of *p*-methylcycloalkylphenols with aminoethylnonylimidazole and alkyimidazoline

This section deals with the production of Mannix bases with a new chemical structure by *p*-methylcycloalkylphenols involved in the aminomethylation reactions of formaldehyde and aminoethylnonylimidazole synthesized by known methods, as well as the modification of *p*-cycloalkylphenols with alkyimidazoles.

Aminomethylation reactions of *p*-methylcycloalkylphenols with aminoethylnonylimidazole

The following are the results of the aminomethylation reaction of *p*- (1-methylcyclohexyl)-phenol with formaldehyde and aminoethyl-nonylimidazoline for an example.



Aminomethylation reactions of *p*-(1-methylcyclohexyl)-phenol

with aminoethylnonylimidazole were carried out by the following method: Fill a three-necked flask with 47.5 g (0.25 mol) of *p*-(1-methylcyclohexyl)-phenol, 60.0 g of aminoethylnonylimidazole, 47.5 g of benzene and heat by stirring. When the reaction temperature reaches 40°C, 25.0 g of formalin is added. The reaction temperature is then raised to 80°C and the mixing is continued at this temperature for another 2 h; then the experiment is carried out using the above methodology.

As a result, 84.6 g of 2-hydroxy-5(1-methylcyclohexyl)-benzylaminoethylnonylimidazole is obtained, which is 76.7% of the yield.

The following groups were found in the IR spectrum of synthesized 2-hydroxy-5(1-methylcyclohexyl)-benzylaminoethylnonylimidazole: in the band 3105-3500 cm^{-1} OH group, 1380 cm^{-1} -CH₃ group, C=C bond of the aromatic ring 1628 cm^{-1} , sliding of the naphthenic ring 830 and 885 cm^{-1} are observed. Benzene ring para replacement was found in 828, 1240, 1590, 1610 and 396 cm^{-1} , NH-group 3050 cm^{-1} , C - N 1095, 1100, 1120 and 1300 cm^{-1} strips.

The following signals are observed in the ¹H NMR spectrum of 2-hydroxy-5(1-methylcyclohexyl)-benzylaminoethylnonylimidazole: the cyclic structure of the substance is in the band $\delta = 1.35\text{-}1.6$ ppm, the signal of the CH₃ group is $\delta = 0.9\text{-}1.1$ ppm, the protons of the aromatic nucleus are $\delta = 6.75$ ppm, the proton of the hydroxyl group attached to the aromatic nucleus is in the band $\delta = 6.5$ ppm, the C=C bond of the cyclohexane ring was observed in the low-intensity $\delta = 5.2\text{-}5.4$ ppm multiplet, the NH-group proton in the $\delta = 3.60$ ppm resonance signal, and the -CH₂- radical proton in the $\delta = 4.70$ ppm band.

Thus, the chemical structure of 2-hydroxy-5(1-methylcyclohexyl)-benzylaminoethylnonylimidazole is fully proven; physical - chemical parameters of the substance were determined.

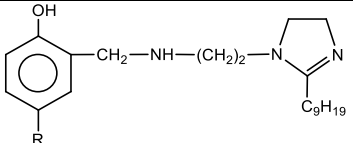
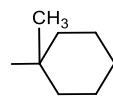
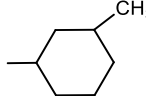
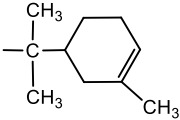
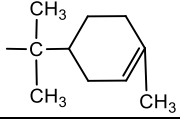
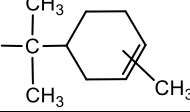
Table 5 shows the physicochemical properties of 2-hydroxy-5(cycloalkyl)-benzylaminoethylnonylimidazole synthesized.

The table shows that the elemental composition of the synthesized 2-hydroxy-5(cycloalkyl)-benzylaminoethylnonylimidazole obtained by laboratory analysis corresponds to the calculated

elemental composition.

Table 5

Physico-chemical properties of 2-hydroxy-5(cycloalkyl) - benzylaminoethylnonylimidazoline

	T _{boil.} , °C (10 mm Hg)	n_D^{20}	ρ_4^{40}	Molecular weight	Calculated, % Found, %		
					C	H	N
R = 	211- 216	1.6107	1.1230	441	$\frac{76.2}{75.6}$	$\frac{10.7}{10.2}$	$\frac{9.5}{8.8}$
	207- 212	1.5965	1.1147	441	$\frac{76.2}{75.4}$	$\frac{10.7}{9.9}$	$\frac{9.5}{8.7}$
	223- 226	1.6673	1.1415	481	$\frac{77.3}{76.6}$	$\frac{10.6}{9.8}$	$\frac{8.7}{8.3}$
	228- 234	1.6726	1.1607	481	$\frac{77.3}{76.4}$	$\frac{10.6}{9.7}$	$\frac{8.7}{7.8}$
	223- 235	1.6705	1.1564	481	$\frac{77.3}{76.5}$	$\frac{10.6}{9.5}$	$\frac{8.7}{8.1}$

Modifications of alkyimidazoles with - *p* - methylcycloalkylphenols

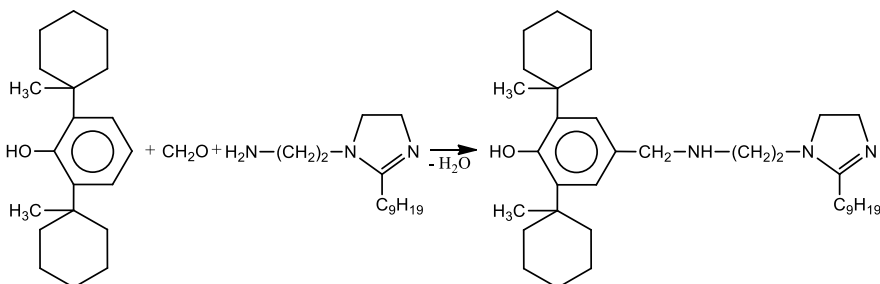
Modifications of *p*-methylcycloalkylphenols in different proportions with alkyimidazoles (NPA: PEPA = 2:1) were prepared.

This section discusses the production of complexes of *p*-methylcycloalkylphenols modified with alkyimidazoles. Modifications of *p*-methylcycloalkylphenols with alkyimidazoline in a 1:1 mass ratio were prepared for the preparation of complexes. IR, ¹H NMR and ¹³C NMR spectra of the obtained compositions were drawn and physic - ochemical properties were determined.

Study of the interaction of space-difficult methylcycloalkylphenols with aminoethylnonylimidazolines

This section discusses the interaction of 2,6-dimethylcycloalkylphenols with formaldehyde and aminoethylnonylimidazole to obtain Mannix bases. Phenols based on 1-methylcyclohexene, 3-methylcyclohexene, isoprene cyclodimers were used as space-difficult cycloalkylphenols.

The results of the aminomethylation reaction of 2,6-di-(1-methylcyclohexyl) -phenol with aminoethylnonylimidazole are given below for an example:



Fill a three-necked flask with 71.5 g of 2,6-di-(1-methylcyclohexyl) -phenol, 60.0 g of aminoethylnonylimidazole, 71.5 g of benzene and mix by heating. When the reaction temperature reaches 40°C , 25.0 g of 30% formaldehyde solution is added dropwise from the separating funnel within 1 hour. The experiment is then continued with the above methodology.

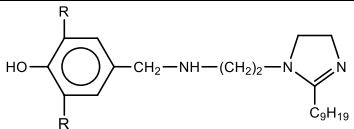
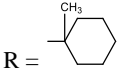
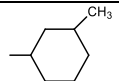
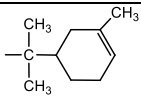
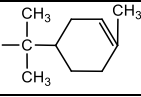
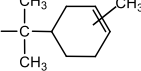
As a result, 96.3 g of 4-hydroxy-3,5-di-(1-methylcyclohexyl)-benzylaminoethylnonylimidazole is obtained this indicates that the yield was 71.7% for the 2,6-di-(1-methylcyclohexyl) -phenol taken.

The synthesis of other 4-hydroxy-3,5-di-(methylcyclohexyl)-benzylaminoethylnonylimidazoleins was also performed.

Table 6 shows the physico - chemical properties and elemental composition of 4-hydroxy-3,5-di-(methylcyclohexyl)-benzyl-aminoethylnonylimidazole.

Table 6

Physico - chemical properties and elemental compositions of 4-hydroxy-3,5-di-(methylcyclohexyl) - benzylaminoethylnonylimidazolines

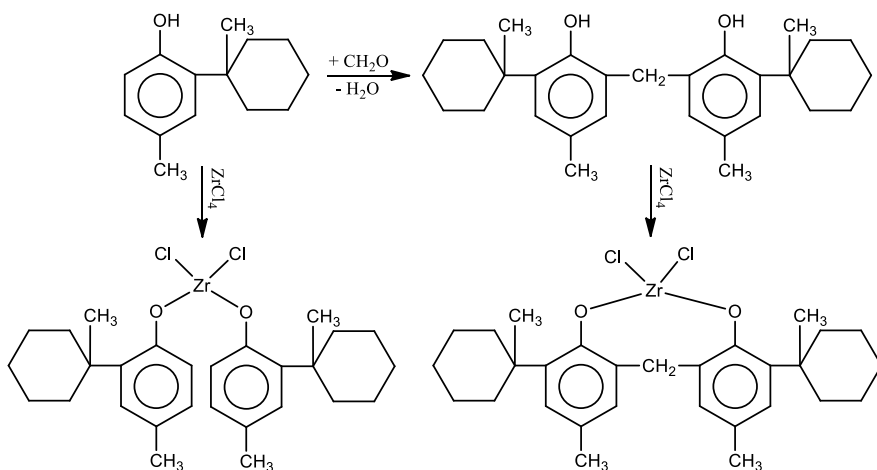
	T _{boil.} , °C (5 mm Hg)	n _D ²⁰	ρ ₄ ⁴⁰	Mol. mas.	Calculated, % Found, %		
					C	H	N
 R = C ₃₅ H ₅₉ N ₃ O	228-233	1.7605	1.186	537	<u>78.2</u> 78.0	<u>11.0</u> 10.5	<u>7.8</u> 7.3
 C ₃₅ H ₅₉ N ₃ O	226-230	1.7128	1.164	537	<u>78.2</u> 77.6	<u>11.0</u> 10.7	<u>7.8</u> 7.2
 C ₃₈ H ₆₃ N ₃ O	231-236	1.7230	1.1710	577	<u>79.0</u> 78.6	<u>10.9</u> 10.3	<u>7.3</u> 7.0
 C ₃₈ H ₆₃ N ₃ O	237-242	1.7847	1.1880	577	<u>79.0</u> 78.2	<u>10.9</u> 10.3	<u>7.3</u> 6.5
 C ₃₈ H ₆₃ N ₃ O	233-240	1.7705	1.1800	577	<u>79.0</u> 77.0	<u>10.9</u> 10.4	<u>7.3</u> 6.5

Areas of application of cycloalkylphenols with aminoethylnonylimidazoline Mannix bases and modifications with alkylimidazole

Testing of 2(methylcyclohexyl)-4-methylphenols as ligands to catalytic precursors used in the process of oligomerization of ethylene

New catalysts for the process of oligomerization of ethylene were synthesized from the interaction of synthesized 2-cycloalkyl-4-methylphenols and their 2,2'-methylenebis products with ZrCl₄ together with the staff of the laboratory №30 of the Institute of Petrochemical Processes of ANAS. It was found that heterogeneous zirconium complexes synthesized on the basis of 2-methylcycloalkyl-4-methylphenols, 2,2'-methylenebicycloalkylphenols and oligomer obtained from the oligomerization of ethylene using (C₂H₅)₂AlCl as a cocatalyst consist mainly of the oligomeric C₄-C₁₀ fraction of α-olefins and this means that the amount of

oligomer product is 80-90%, depending on the composition of the ligand and the direction of the reaction. Zirconium complex based on 2,2'-methylenebis-[4-methyl-6(1-methylcyclohexyl)phenol] obtained from the synthesized ligands and as a catalyst (C_2H_5) in the presence of $AlCl_3$, in aliphatic solvents (isooctane, heptane, hexane, etc.) and catalytic system Al : Zr = (25-30):1 mol and at a pressure of 1.8-5.0 MPa, at a temperature of $90^\circ C$ consists of a fraction of polyethylene oil with a yield of 57.5-67.5% of the converted ethylene.



As a result of research, it was determined that when methylcyclohexyl-4-methylphenols are used as ligands to the catalysts used in the oligomerization reaction of C_4 - C_{10} olefins, they are 88-91% higher than the target products, the yield on known catalysts is 70-75%.

Let's look at the results of oligomerization of ethylene in the presence of a catalytic system based on mono-phenolate chloride zirconium precursors.

Experimental results show that in the presence of the catalytic system $[2(1-methylcyclohexyl)-4-methylphenolate]_2ZrCl_2$ and $(C_2H_5)_2AlCl$ (Al/Zr mol ratio - 20) at a temperature of $70^\circ C$ the yield of the C_6 - C_{10} fraction is 65.3% by mass of converted ethylene. When using $[2,6-di-triple-butyl-4-methylphenolate]_2ZrCl_2$ known for this purpose the yield of the C_6 - C_{10} fraction is 48.0% for the converted

ethylene.

It was determined that in the process of oligomerization of ethylene in the presence of a catalytic system based on the precursor of 2,2'-methylene bisphenolic chloride zirconium synthesized on the basis of bisphenol obtained from the condensation of 2(1-methylcyclohexyl)-4-methylphenol with formaldehyde, when using this catalyst, the main product of the oligomerization reaction of ethylene is the C₆-C₁₀ linear α -olefins fraction.

In the presence of a known catalytic system consisting of 2,2'-methylenebis- (4-methyl-2-triple-butylphenolate) ZrCl₂ and (C₂H₅)₂AlCl, in the ratio Al/Zr= 20, the pressure of ethylene is 30 MP, the reaction temperature is 70°C, - the yield of the C₆ - C₁₀ oligomer fraction is 69.6% for converted ethylene. The composition of the fraction of oligomers C₄ and C₁₂-C₁₈ is 22.4 and 8.0% by weight, respectively. The content of α -oligomers in the fraction of C₆-C₁₀ oligomers reaches 99.0%.

When using 2,2'-methylenebis- [4-methyl-6(1-methylcyclohexyl)-phenolate] ZrCl₂ ligand synthesized on the basis of bisphenol obtained, the yield of C₆-C₁₀ oligomer fraction increases to 77.5% for converted ethylene. In this case, the yield of ethylene-butene-1 dimer fraction is significantly reduced and is 14.2% by weight.

Thus, it can be concluded that Zr-phenolates obtained on the basis of 2(1-methylcyclohexyl)-4-methylphenol and 2,2'-methylenebis-[4-methyl-6(1-methylcyclohexyl) phenol] are catalytic agents used in the oligomerization of ethylene. They are much superior and more effective than other known ligands used for this purpose as ligands to precursors. Therefore, they can be used as ligands for catalytic precursors used in the oligomerization process of ethylene.

Tests of benzylphenylamines as antioxidants in CKN-26 nitrile rubber

5 samples of antioxidants presented by us in the Central Laboratory of Sumgayit "Synthesis Rubber" Plant - 2-hydroxy-5-(1-methylcyclo-hexyl)-benzylamine (sample 1); 2-hydroxy-3-(1-methyl-cyclohexyl) -5-methylbenzylphenylamine (sample 2); 2-hydroxy-5-methylbenzyl-2,6-di-isopropylphenylamine (sample 3); 2-

hydroxy-5- (1-methylcyclohexyl) -benzyl-2,6-di-isopropylphenylamine (sample 4); samples of 2-hydroxy-3-(1-methylcyclohexyl)-5-methylbenzyl-2,6-di-isopropylphenylamine (sample 5) and HG-2246, which are widely used in industry for this purpose, were tested as antioxidants in CKN-26 nitrile rubber.

The antioxidant quality of the samples was determined during the thermodestruction of the rubber and its aging process under natural conditions for 6 months.

CKN-26 nitrile rubber with the following properties was used for the test: According to Shtaudinger, the average molecular weight was $56.5 \cdot 10^3$, unsaturation - 1.98%. The samples were prepared by mixing a calculated amount of known and presented antioxidants with rubber in a cold waltz.

Each sample was then coated on a 20×80 mm glass $1 \div 1.5$ mm thick. For comparison, nitrile rubber with no antioxidant added and antioxidant added was used. Medium-viscosity molecular weights of rubber were determined according to Staudinger before and after the test of all samples. Thermodestruction was carried out at atmospheric pressure for 2 hours at a temperature of 150°C in a special chamber.

The quality indicators of the presented antioxidants are given in Table 7.

Table 7

Test results of antioxidant samples in CKN-26 nitrile rubber (AO amount - 0.2%)

Names of antioxidants	Molecular weight according to Staudinger, $\times 10^3$			Stability coefficient after thermodestruction	Stability coefficient after 6 months
	Initial	After thermodestruction $t = 150^\circ\text{C}$ $\tau = 2$ hours	After 6 months in natural conditions		
CKN-26 brand rubber (without AO addition)	56.5	23.2	51.0	0.41	0.90
CKN-26 + NG-2246	56.5	33.4	53.5	0.59	0.95
CKN-26 + example 1	56.5	48.5	53.0	0.86	0.94
CKN-26 + example 2	56.5	50.1	54.2	0.89	0.96
CKN-26 + example 3	56.5	47.3	52.7	0.84	0.93
CKN-26 + example 4	56.5	52.8	56.5	0.93	1.0
CKN-26 + example 5	56.5	53.6	56.5	0.95	1.0

As can be seen from the table, sample 4 and sample 5 have positive quality characteristics compared to NG-2246, which is used as an antioxidant for nitrile rubber in industry, and can be presented as an antioxidant for CKN-26 nitrile rubber.

Tests of 2-hydroxy-3 methylcyclohexylbenzylaminoethyl-nonylimidazoles as a high temperature resistant antioxidant in M-8 engine oil

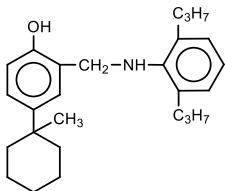
The quality of synthesized 2-hydroxy-3(methylcycloalkyl)-5-methylbenzylaminoethyl-nonylimidazole was assessed by the amount and viscosity of sediment formed after oxidation of oil in M-8 engine oil at 200°C in accordance with ГOCT 11063-77. The amount of antioxidants was taken as 0.5%.

The tests were performed on a DK-NAMI device and the kinetic viscosities of the samples before and after oxidation for 20 hours were determined, and the effectiveness of antioxidants for increasing the viscosity was evaluated.

The results of the tests of cycloalkylbenzylkyimidazole as an antioxidant (AO) in M-8 engine oil are given in Table 8.

Table 8

Results of tests of 2-hydroxy-3(methylcycloalkyl)-5-methylbenzylaminoethylimidazoles as an antioxidant (AO) in M-8 engine oil

Ordinal numeral	Names	Sediment, %	Viscosity, mm ² /sec, at 100°C-		Δv, %
			test		
			before	after	
1	2	3	4	5	6
1.	M-8 engine oil (AO without adding)	4.47	7.95	9.23	16.10
2.	M-8 + ionol (known)	1.36	7.97	9.24	15.93
3.	M-8 +  (known)	1.33	7.90	9.13	15.57

continuation

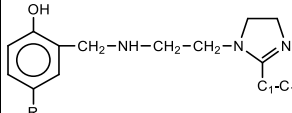
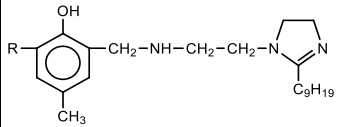


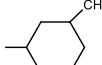
1	2	3	4	5	6
4.	<p>M-8 +</p>  <p>(known)</p>	0.72	7.98	9.20	15.29
5.	 <p>where R =</p> 	0.40	7.96	9.12	14.57
6.		0.34	7.93	8.97	13.11
7.		0.38	7.95	9.06	13.96

Table 8 shows that the cycloalkylbenzylonylimidazolines give a small (0.34-0.40%) precipitate after 20 hours of oxidation at 200°C compared to other known industrially used ionol and 2-hydroxy-5-alkylbenzylaminoethylalkylimidazole antioxidants, the increase in viscosity is 13.11-14.57%, which ensures the use of 2-hydroxy-3 (methylcycloalkyl)-5-methylbenzylaminoethylalkylimidazoline as an antioxidant for M-8 engine oil.

Tests of modifications of oxyethylated nonylphenol with alkylimidazoles as a conservation for corrosion protection of metals

The samples were prepared using the following methodology and tested as a conservation .

For this purpose, oxyethylated *para*-nonylphenol (ONP) with alkylimidazole (NPA:PEPA = 2:1) was prepared at room temperature in 3 different ratios (1:2, 1:1, 2:1 mass ratio): Complex-I - imidazoline : ONP = 2:1; Complex-II - imidazoline: ONP = 1:1; Complex-III – imidazoline : ONP = 1:2.

Samples of T-30 oil in different proportions (5 and 10%) were

prepared to test the inhibitory properties of the obtained complexes as a conservation liquid:

Example I– T-30 oil distillate (95g) + Complex -I (5g) = 95%:5%

Example II– T-30 oil distillate (90g) + Complex -I (10g) = 90%:10%

Example III–T-30 oil distillate (95g) + Complex -II (5g) = 95%:5%

Example IV–T-30 oil distillate (90g) + Complex-II (10g) = 90%:10%

Example V– T-30 oil distillate (95g) + Complex-III (5g) = 95% : 5%

Example VI–T-30 oil distillate (90g) + Complex-III (10g)=90%:10%

Tests were carried out in accordance with ГOCT 9054-75. Metal plates made of “steel-3” with a size of 40-50 mm ± 0.3 and a thickness of 5.5 mm were used to perform the test studies. The surface of the metal plates was cleaned, polished and used after wiping and drying with organic solvents (gasoline or alcohol). The cleaned metal boards were hung on a polymer thread for 24 hours in a prepared conservation liquid, then removed and stored in atmospheric air for 1 hour and tested in seawater, 0.001% H₂SO₄ solution and a thermo-humidification chamber.

The operating mode of the “Q-4” thermo-humidification chamber used as an aggressive environment was as follows: it operated for 8 hours at a temperature of 40 ± 20C and a humidity of 95 ± 3%, then stopped for 16 hours (with periodic condensation). Tests were repeated three times in each conservation fluid and surface corrosion was checked daily by observing the metal boards.

The test results are given in Table 9

Table 9

Results of tests of imidazoline : ONP complexes in T-30 oil distillate as conservation liquid in different proportions

№	Examples	With %-	«Q-4» in the hydraulic chamber	In the sea water	In 0,001% H ₂ SO ₄ solution
1	2	3	4	5	6
Example I	T-30 oil distillate + Complex-I	5	62	55	55
Example II	T-30 oil distillate + Complex -I	10	74	62	55
Example III	T-30 oil distillate + Complex -II	5	41	51	51

continuation

1	2	3	4	5	6
Example IV	T-30 oil distillate + Complex -II	10	41	51	46
Example V	T-30 oil distillate + Complex -III	5	41	51	46
Example V	T-30 oil distillate + Complex -III	10	41	55	55

It is clear from the table that a positive result cannot be achieved by increasing the amount of ONP in the complex. Complex-I (imidazoline : ONP = 2:1) shows a more effective result than other complexes.

Determination of surface tension of oxyethylated nonylphenol composition with alkylimidazolines (ONP + AIM)

The surface tension of aqueous solutions of the prepared ONP+AIM composition (95:5 weight ratio) of different concentrations (0.25, 0.5 and 1.0%) was determined at the water-air boundary using a Du Nui ring using a Sigma 702 (Finland) tensiometer. As a result of the research, it was determined that the obtained substance has a fairly high surface activity (Table 10) and reduces the surface tension at that limit from 71.7 mN/m (without SAM) to 30.3 mN/m.

Table 10
Values of surface tension of aqueous solutions of ONP + AIM (90:10 mass ratio) at the air border

Concentration of the substance, % (by mass)														
0.000025	0.00005	0.0001	0.00025	0.0005	0.001	0.0025	0.005	0.01	0.025	0.05	0.1	0.25	0.5	1.0
Surface tension at the water-air boundary, mN/m (at 25 °C)														
65.5	63.4	58.7	50.1	46.1	46.0	33.5	32.0	31.2	30.5	30.3	30.4	30.3	30.3	30.3

Note: Surface tension of water 71.1 mN/m (without SAM)

As can be seen from the table, as the density of SAM increases, the value of surface tension decreases and the value of surface tension at higher density stabilizes. The fact that the value of surface tension does not change with increasing concentration of SAM at

high concentrations indicates the formation of micelles in the solution and the stabilization of the colloidal properties of the solution.

Surface tension of aqueous solutions of the prepared ONP+AIM composition with different concentrations (0.000025, 0.00005, 0.0001, 0.00025, 0.0005, 0.001, 0.0025, 0.005, 0.01, 0.05, 0.1, 0.25, 0.5 and 1.0%) in the ratio of 90:10 mass at the water-air boundary determined using the methods described above.

As can be seen from table 10, the surface tension of aqueous solutions of different concentrations over a very wide range (0.000025 - 1.0%) was lower than the surface tension of water (71.1 mN/m). This confirms that the modification of oxyethylated nonylphenol with alkylimidazoline is a highly surfactant.

The values of surface tension at the boundary between air and aqueous solutions of the prepared composition were determined and surface tension isotherms were established (Figure 11).

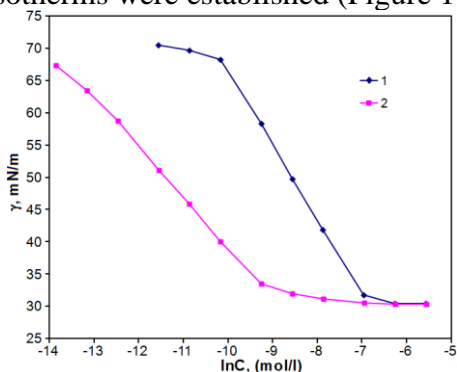


Figure 11. Graphs of dependence of surface tension on natural logarithmic density of aqueous solutions of surfactant (25°C): 1. (95:5 mass ratio) 2. (90:10 mass ratio)

As can be seen from the figures, the values of surface tension decrease sharply as the concentration of the surfactant in the solution increases. After a certain hardness, the values of surface tension do not change, ie stabilization is observed. The density at which stabilization begins is taken as the value of the critical mycelial formation density (CMF) Table 11. As can be seen from the table, when the share of AIM in the surface-active composition increases from 5% to 10%, the cost of KMG decreases by 10 times.

Colloid-chemical parameters of surfactant compositions are given in Table 11.

Table 11

Surface activity parameters of surfactant composition

Surface-active composition	β	$\Gamma_{\max} \times 10^{10}, \text{ mol} \cdot \text{cm}^{-2}$	$A_{\min} \times 10^2, \text{ nm}^2$	$\text{KMG} \times 10^3, \text{ mol} \cdot \text{dm}^{-3}$	$\pi_{\text{KMG}}, \text{ mN} \cdot \text{m}^{-1}$	$\Delta G_{\text{mic}}, \text{ kJ} \cdot \text{mol}^{-1}$	$\Delta G_{\text{ad}}, \text{ kJ} \cdot \text{mol}^{-1}$
95:5 mass ratio	0,387	2,30	72,2	1,5	41,6	-22,34	-24,15
90:10 mass ratio	0,779	1,57	106,0	0,15	41,7	-38,80	-41,47

As can be seen from the table, as the share of AIM in the composition increases, the value of G_{\max} decreases and the value of A_{\min} increases. Due to the large number of hydrophilic polar groups in AIM, its share in the composition is already increasing the value of A_{\min} .

In these compositions, the value of π_{KMG} varies in the range of 41.6-41.7 mN/m. The increase in the share of AIM in the composition has led to a slight increase in the price of π_{KMG} .

The degree of reverse ion binding (β) was calculated based on the concentration-dependent curves of the specific electrical conductivity of aqueous solutions of the prepared surfactants (Figures 12 and 13):

$$\beta = 1 - \alpha = 1 - S_2/S_1$$

where α is the degree of dissociation of the reverse ion of the surfactant, S_1 is the ratio of dk/dC to the concentration of KMG, and S_2 is the ratio of dk/dC after the concentration of KMG.

The values of the standard Gibbs energy of the micellar formation process at a given temperature using the values of KMG and β of surfactant compositions were calculated using the following formula:

$$\Delta G_{\text{mic}} = (1 + \beta)RT \ln X_{\text{KMG}}$$

where X_{MMG} is the molar fraction in KMG, β -degree of reverse ion binding, R is the universal gas constant, and T is the absolute temperature (298 K).

The values of the Gibbs standard energies of the adsorption process at the water-air boundary of surfactants are calculated by the following formula:

$$\Delta G_{\text{ad}} = (1 + \beta)RT \ln X_{\text{KMG}} - 0.6023 \pi_{\text{KMG}} A_{\text{KMG}}$$

Figure 12 shows the Gibbs energies of the formation of surfactants in an aqueous solution and the adsorption processes at the water-air boundary. As can be seen, the values of the standard Gibbs energies of both mycelial formation and adsorption processes are negative. Thus, in these SAMs, the processes of micellar formation and adsorption occur spontaneously. Figures 12 and 13 show that when the share of AIM in the composition increases from 5 to 10%, the prices of ΔG_{mic} and ΔG_{ad} decrease. Thus, the increase in the share of AIM in the composition has a positive effect on mycelial formation and adsorption processes.

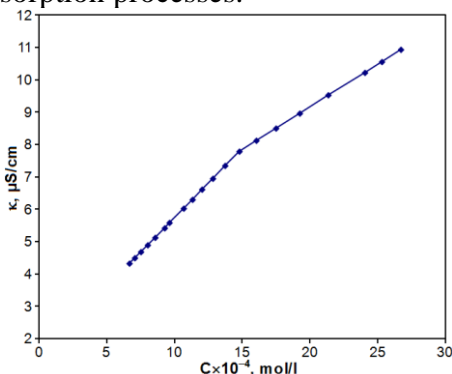


Figure 12. Density dependence of the specific electrical conductivity of an aqueous solution of a surfactant composition in the mass ratio ONP:AIM = 95: 5 (25°C)

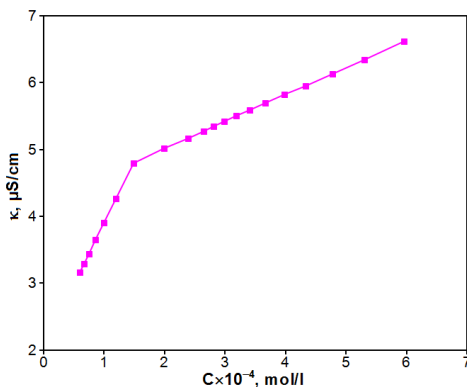


Figure 13. Density dependence of the specific electrical conductivity of an aqueous solution of a surfactant composition in the ratio of ONP:AIM = 90:10 (25°C)

Study of modifications of oxyethylated nonylphenol with alkyimidazoline as a CO₂ corrosion inhibitor

The properties of oxyethylated nonylphenol modifications with alkyimidazole as a corrosion inhibitor in the CO₂ environment were studied in the ACM GILL AC potentiometer using the ACM program. Corrosion rates of electrodes without inhibitors and compositions at 50°C for 5 h were determined. The protective properties of the studied compounds were studied at a concentration of 50, 100 and 150 mg/l. The results of the protection of the synthesized alkyimidazole compositions obtained with ONP in mass ratios of 5:95; 10:90 are given in Figures 14 and 15.

At the same time, depending on the concentration of the studied imidazoline salts in the CO₂ environment, the surface-coating coefficients, adsorption constant and Gibbs energies were calculated (Table 12).

It was found that ONP compositions with alkyimidazole at a concentration of 50-150 mg/l protect the metal surface from corrosion by 93.5-99.5%. The fact that these compounds have Gibbs energies below -35 kC indicates that they form a durable coating on the surface due to chemical adsorption.

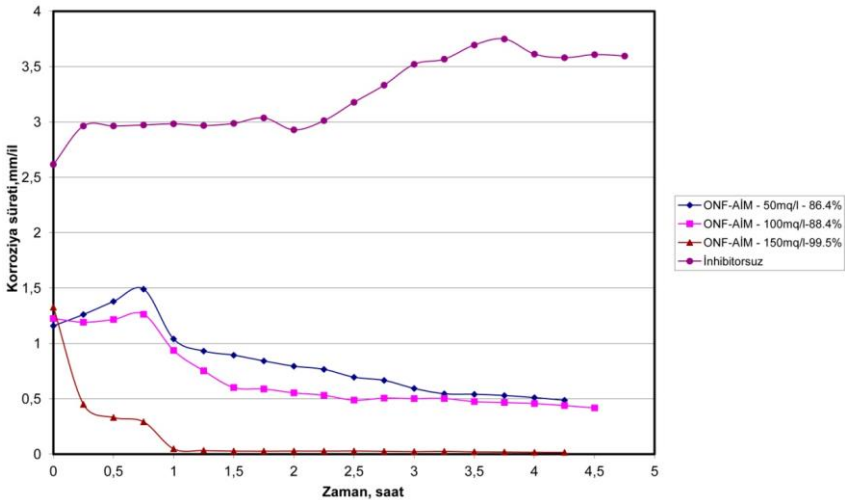


Figure 14. Time dependence of the corrosion rate in CO₂ medium of the composition of alkyimidazole obtained with ONP in the ratio of 5:95 mass

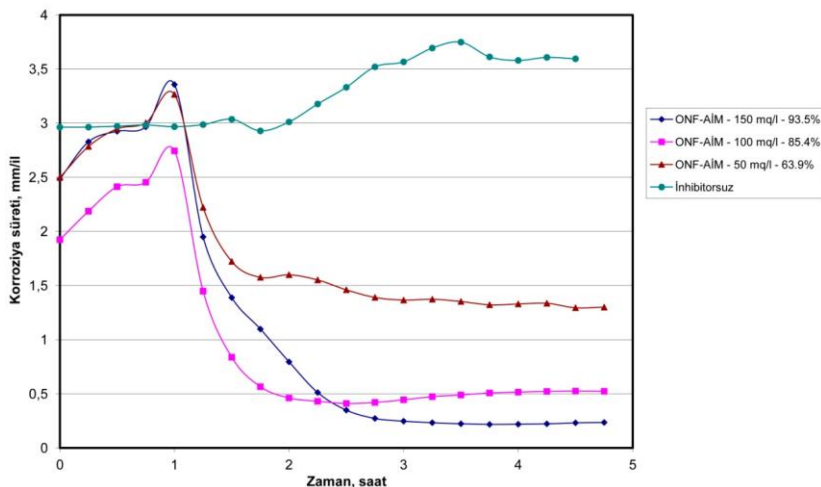


Figure 15. Time dependence of corrosion rate in CO₂ environment of the composition of alkylimidazole obtained by mass of 10:90 with ONP

Table 12

Calculated results of ONP compositions with alkylimidazole in CO₂ environment

Synthesized reagent	Concentration C, (mg/l)	Corrosion rate, ρ , mm/y	Surface coverage coefficient, θ	Adsorption constant, K, M ⁻¹ ·10 ⁴	Protection effect Z, %	Gibbs energy, ΔG_{ads}^0 kC/mol ⁻¹
Without inhibitors	–	3.59	–	–	–	–
Composition of alkylimidazole with ONP (5:95 by weight)	50	0.47	0.87	8.8	86.9	-38
	100	0.42	0.88	5.1	88.3	-37
	150	0.02	0.99	79.0	99.4	-44
Composition of alkylimidazole with ONP (10:90 by weight)	50	1.3	0.64	2.3	63.8	-35
	100	0.52	0.86	3.8	85.5	-38.5
	150	0.23	0.94	6.7	93.6	-37

Study of the effect of oxyethylated nonylphenol compositions with alkylimidazoles against sulfate-reducing bacteria

The effect of SRB on the incubation period of 15 days of

compositions prepared in ONP and AIM 95:5, 90:10 and 50:50 mass ratios was studied as follows. Reagent-free and reagent media were used for comparison. 1 ml of the bacterial medium was diluted with sterile water and simultaneously transplanted into a Posgate B nutrient medium in 10 ml test tubes in a 1:9 ratio and kept in a thermostat at 30-35°C for 15 days to determine the number of bacteria growing in the medium. In the end, the number of bacteria in the non-inhibitor medium taken under microscopic control was $n=10^8$ cell number/ml, and in the inhibitory medium in the concentration of 50 mg/l in all three samples (composition-1, composition-2, composition-3) the number of bacteria $n=10^1$ cell number/ml was determined (Table 13).

Table 13

Results of bactericidal effect of ONP and AIM modifications at different concentrations

Conventional name and composition of complexes	Concentration of substance, C, mg/l	Number of bacteria (cell number/ml)	The amount of H ₂ S, mg/l	Bactericidal effect, Z, %
Composition -1 (ONP:AIM = 95:5 mass ratio)	50	10 ¹	86	77
	150	10 ¹	39.5	89.4
	250	10 ¹	19	95
Composition -2 (ONP:AIM = 90:10 mass ratio)	50	10 ¹	17.2	95.4
	150	10 ¹	7	98.1
	250	-	-	100
Composition -3 (ONP:AIM = 50:50 mass ratio)	50	10 ¹	4.5	98.8
	150	10 ¹	3.2	99.1
	250	-	-	100
Control -I The amount of H ₂ S in an environment without SRB	24 mg/l			
Control-II The amount of H ₂ S in an environment with SRB	375 mg/l			
Control-III the number of bacteria in the nutrient medium	10 ⁸ cell number/ml			

Studies have shown that hundreds of millions of bacteria (10^8) have developed in an inhibitor-free environment. In inhibitory media, the number of bacteria in the samples taken at 50, 150 and 250 mg/l was as follows:

In Composition 1 (ONP:AIM = 95:5 mass ratio), the number of bacteria decreased from 10^8 to 10^1 at a concentration of 50 mg/l (the number of bacteria increased from 10 to 100 million) and from 10^8 to 10^1 at a concentration of 150, at a concentration of 250 mg/l, fell from 10^8 to 10, partially stopping the life activity of bacteria.

In Composition 2 (ONP:AIM = 90:10 mass ratio), the number of bacteria decreased from 10^8 to 10^1 at a concentration of 50 mg/l and from 10^8 to 10^1 at a concentration of 150 mg, at a concentration of 250 mg/l, it dropped from 10^8 to 0 and completely stopped the life of bacteria.

In Composition 3 (ONP:AIM = 50:50 mass ratio), the number of bacteria dropped from 10^8 to 10^1 at a concentration of 50 mg/l and from 10^8 to 10^1 at a concentration of 150 mg, at a concentration of 250 mg/l, it dropped from 10^8 to 0 and completely stopped the life of bacteria.

RESULTS

1. For the first time, alkylation reactions of *p*-cresol with KU-23 and orthophosphate acid-impregnated zeolite-Y catalysts with 1- and 3-methylcyclohexenes, cyclodimers of isoprene were studied in intermittent and uninterrupted devices and the effect of various kinetic parameters (temperature, time, mole ratios of components, amount of catalyst, volume, velocity) on the yield and selectivity of the target products - 2-methylcycloalkyl-4-methylphenols. It was determined that under the found optimal conditions of alkylation reactions ($t = 115-140^\circ\text{C}$; $\tau = 4-6$ s; 1:1 mol; cat. 10-15%), the yield in the intermittent device for *p*-cresol is 66.7-82.4%, for the target product. According to the selectivity is in the range of 87.9-95.7%, and in the pilot device operating continuously ($t = 120-140^\circ\text{C}$; $V = 0.5$ s⁻¹; 1:1 mol), the yield is

- 55.7-67.3%, respectively, and the selectivity is 84.5-96.1% [1, 3, 5, 10, 13, 14, 15, 30, 31, 32].
2. Aminomethylation reactions of obtained 2-methylcyclohexyl-4-methylphenols with formaldehyde and aminoethylnonylimidazole were studied. It was determined that 2-hydroxy-3(methylcyclohexyl)-5-methylbenzylaminoethylnonyl imidazolines were obtained under optimal conditions of aminomethylation reactions: at 80°C for 2-2.5 hours with a yield of 66.5-79.3% [16, 18, 20, 23, 26, 33].
 3. Interactions of *p*-methylcyclohexylphenols with formalin and aminoethylnonylimidazole were performed. It was determined that the yield of aminoethylation reactions at 80°C, Mannix bases obtained in 2-3 hours - 2-hydroxy-5(methylcyclohexyl)-benzylaminoethylnonyl-imidazole is 63.4-76.7% (for *p*-cyclohexyphenols) [4, 6, 19, 24, 28, 35, 39, 41].
 4. Aminomethylation reactions of space-difficult methylcycloalkylphenols with formaldehyde and aminoethyl-nonylimidazole were carried out. Under the optimal conditions of the studied reactions, the yield of target products - 4-hydroxy-3,5-dimethylcycloalkylbenzyl-aminoethylnonylimidazole is 61.3-71.7% (for 2,6-dimethylcyclo-alkylphenol) [11, 17, 25, 27].
 5. Interactions of natural petroleum acid (NPA) with polyethylene polyamine (PEPA) were first performed in nitrogen. The reactions were carried out in the ratio of NPA: PEPA = 2:1 mol, at 140°C for 3-3.5 hours, then by raising the reaction temperature to 235-240°C for 2-2.5 hours with the separation of water in both cases. It has been established that 95-96% of alkylimidazole is obtained under these conditions [40].
 6. Complex compounds obtained from the interaction of 2-methylcycloalkyl-4-methylphenols and 2,2'-methylenebicycloalkyl-4-methylphenols with ZrCl₄ at different molar ratios were tested in the process of oligomerization of ethylene as a ligand to heterogeneous metal complex catalytic precursors. It was determined that 2,2'-methylenebis[6(1-methylcyclohexyl)-4-methylphenolate] in the presence of a catalytic system consisting of ZrCl₂ and (C₂H₅)₂AlCl, in the ratio Al/Zr = 20, ethylene

pressure 30 MPa, reaction temperature 70°C The yield of C₆-C₁₀ oligomer fraction is 77.5% for converted ethylene, the catalyst yield is 5543.8 g/h for 1 g Zr, the amount of α-oligomers in C₆-C₁₀ oligomer fraction is 99.5% [7, 38].

7. The 2-hydroxy-3(methylcycloalkyl)-5-methylbenzylphenylamines obtained on the basis of synthesized 2-methylcyclohexyl-4-methyl-phenols were extracted as antioxidants in CKN-26 nitrile rubber comparable to NG-2246, a widely used industrial additive for this purpose. It was determined that the molecular weight of the presented samples after 2 hours in a special chamber at 150°C after thermodestruction was 47.3 - 53.6·10³ and after 6 months the coefficient of stability was 0.93-1.0, which gave rise to their use as an antioxidant in CKN-26 rubber [18, 19, 22].
8. 2-Hydroxy-3(methylcycloalkyl)-5-methylbenzylaminoethylalkylimidazolines have been tested as a high temperature resistant antioxidant for M-8 engine oil. It was found that when 0.5% of freshly synthesized products are added to M-8 engine oil, a small (0.34-0.40%) precipitate is obtained after 20 hours of oxidation, the viscosity increase is 13.11-14.57% [8, 21, 22, 36, 37].
9. Interactions of NPA and PEPA were carried out in a nitrogen environment in a pilot plant with a reactor capacity of V=200 kg installed at the "Tural-110" research and production facility. Reactions were carried out at a ratio of NPA: PEPA = 2:1 mol at 140°C for 3-3.5 hours, then by raising the reaction temperature to 235-240°C for 2.5-3.0 hours. The yield of alkylimidazole obtained under these conditions was 92-94%. Modifications of alkylimidazole to oxyethylated p-nonylphenol in various proportions have been obtained [40, 42].
10. Modifications of obtained 2(methylcyclohexyl)-4-methylphenols, p- and 2,6-di-methylcyclohexoxyphenols with alkylimidazoles in different proportions (2:1; 1:1; 1:2) were prepared with T-30 oil distillate 5-10% - compositions were obtained and tested as conservation liquids. It was found that samples prepared with AIM: ONP=2:1 ratio of the complex with T-30 oil distillate in concentrations of 5-10% give effective results [7].

11. The properties of oxyethylated nonylphenol modifications with alkyimidazoline as a corrosion inhibitor in the CO₂ environment have been studied. As a result of laboratory experiments, it was found that ONP compositions with alkyimidazole, studied in acidic environments saturated with CO₂, show high inhibitory properties. It was found that ONP compositions with alkyimidazole at a concentration of 50-150 mg/l protect the metal surface from corrosion by 93.5-99.5% [12, 34].
12. The effect of oxyethylated nonylphenol modifications with alkyimidazoles (AIM: ONP=5:95; AIM: ONP=10:90 and AIM: ONP=50:50 by weight) against sulfate-reducing bacteria was studied and determined that, the number of bacteria in all three samples at a concentration of 50 mg/l ranged from 10⁸ to 10¹ cell numbers/ml; AIM: ONP=10:90 and AIM: ONP=50:50 in mass ratios at a concentration of 250 mg/l, falling from 10⁸ to 0, completely stopped the life of bacteria [29, 42].
13. Compositions of oxyethylated *p*-nonylphenol with alkyimidazoline in different concentrations were prepared and tested as a surfactant. It was determined that the obtained compositions have a high surface activity. Thus, when they are added by 0.5-1.0% by weight, they reduce the surface tension at the water-air boundary from 71.7 mN/m (without SAM) to 30.3 mN/m [40].
14. Technical and economic indicators of modifications of alkyimidazoles with oxyethylated *p*-nonylphenol were calculated for 3 different options: for option I (ONP: AIM = 95:5 mass ratio) 2555.05 AZN/ton; on option II (ONP: AIM=90:10 mass ratio) 2579.1 AZN/ton; According to option III (ONP: AIM=50:50 mass ratio) it is possible to get 2771.5 AZN/ton profit.

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The defense will be held on 20 October 2023 at 10⁰⁰ at the meeting of the Dissertation council BED 1.17 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev of the Ministry of Science and Education of the Republic of Azerbaijan.

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Dissertation is accessible at the library of the Institute of Petrochemical Processes named after acad. Y.H. Mammadaliyev of the Ministry of Science and Education of the Republic of Azerbaijan.

Electronic version of the abstract is available on the official website of the www.nkpi.az

Abstract was sent to the required addresses on 19 September 2023.

Signed for print: 14.09.2023

Paper format: A5

Volume: 76400

Number of hard copies: 20