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ABSTRACT

of the dissertation for the degree of
Doctor of Science

OBTAINING CONSERVATIVE FLUIDS BASED ON PHENOLFORMALDEHYDE OLIGOMERS MODIFIED BY AMINES, CONTAINING IMIDAZOLINE FRAGMENTS

Specialty: 2314.01 - Petrochemistry

Field of science: Technical science

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INTRODUCTION

Relevance and degree of development of the dissertation work. Corrosion is one of the most widespread types of destruction, as it occurs wherever metal structures are processed or operated. Metal corrosion control is an important direction of technical, economic and environmental activities. There are many options to protect metallic constructions from corrosion process: the use of stainless metal alloys, paint and varnish coatings, protective materials among which corrosion inhibitors have a special place. Adsorption of compounds with an inhibitory effect on the metal surface, where the adsorption-active centers function, occurs not only due to physical van der Waals forces, but also due to chemisorption, i.e. interaction of compounds and exposure to chemical changes in their particles. In this regard, the search and selection of materials, as well as ways to reduce corrosion, doesn't lose its relevance. The lack of a unified theory of corrosion protection indicates the demand for further research in this area. Simultaneously, the main attention is paid to the influence of the functional groups in their composition, the availability of a cheap raw material base, stability, and manufacturability in application. For the purpose of the protection against corrosion of equipment subjected to long-term transportation and storage, conservative fluids and lubricants are used, which in turn are obtained on a petroleum basis, and, as a rule, with the use of oil-soluble corrosion inhibitors. Among the wide variety of such compositions, the role of those based on phenol and its derivatives is very important, which is associated with the existence of a real raw material base - oil, gas, inexhaustible reserves of coal, the possibility of carrying out similar transformations and modifications, and the availability of technological modes. Many of the areas, for example, paint and varnish industry, production of film-forming compositions, etc., where they are widely used, are determined by their protective effect. From the point of view of the search and production of highly effective corrosion inhibitors with a set of required properties, development of methods for modifying polycondensation products of phenol and its alkyl-substituted derivatives with formaldehyde with nitrogen-containing organic compounds is of great importance. The

presence of phenolic hydroxyl and methylol groups, as well as aromatic nuclei with a delocalized six-electron cloud, has a positive effect on the adhesion properties on the metal surface, forming a protective layer, and therefore on the inhibiting characteristics of phenol-formaldehyde oligomers. The advantage of the latter as modifiers mainly lies in the saturation with polar fragments, reactivity, high thermal stability, as well as ensuring the environmental safety of products.Thus, modification of PhFO with nitrogen-containing compounds contributes to the search and expansion of a number of compounds of similar composition with high performance properties on the basis of mainly local, available, inexpensive resources of relevance.

The aim and objectives of the dissertation work. The aim of the dissertation is developing a process for the production of phenol and monoalkyl(C_8-C_{12})phenolformaldehyde (APhFO) oligomers modified by amines containing imidazolines fragments based on distilled natural petroleum acids (DNPA), fatty acids obtained from various vegetable oils, synthetic petroleum acids (SPA), individual carboxylic acids and polyamines (diethylenetriamine -DETA, triethylenetetraamine - TETA, polyethylenepolyamine -PEPA), study and determination of scientific theoretical foundations of the process, determination of the structure of oligomers, physicochemical and thermal properties, study of molecular weight distribution, study of the dependences of various parameters on the composition of oligomers, use of these products as a component of conservative fluids. The following tasks were solved to achieve the set goals in the dissertation work:

- fractionation of polyamines, separation of acids from various vegetable oils (sunflower, cottonseed, corn, soybean, palm) and study of their physical and chemical properties;
- synthesis of amines with imidazolines fragments based on DNPA, fatty acids of vegetable oils (sunflower, cottonseed, corn, soybean, palm), synthetic petroleum acids, individual unsaturated and saturated acids by the example of oleic and palmitic with polyamines - DETA, TETA, PEPA;
- synthesis of amidoamines based on DNPA and polyamines -

DETA, TETA, PEPA;

- development of a process for obtaining phenol and monoalkyl (C_8-C_{12})phenolformaldehyde oligomers (PhFO and APhFO) modified by imidazolines and amidoamines of various qualitative and quantitative composition, optimization of the synthesis process;

- study of the structure of the synthesized oligomers and the proposed mechanism for the process;

- determination of the physicochemical properties of synthesis products and solubility in polar and non-polar solvents;

- study of molecular weight distribution of the synthesized oligomers by gel-permeation chromatography, study of the regularities of changes in thermal stability depending on qualitative and quantitative composition of nitrogen-containing phenolic oligomers, conclusions and substantiation of destructive properties and thermal effects;

- study of the inhibiting properties of phenol- and monoalkyl (C_8-C_{12})phenol-formaldehyde oligomers modified by amines containing imidazolines fragments and amidoamines of various qualitative and quantitative compositions in T-30 turbine oil, study of the anticorrosive properties of conservative fluids of various compositions, conclusions, comparison and substantiation of the results.

Research methods. The scientific results from the dissertation were proved by the contemporary physical research methods as IR- spectroscopy (on "ALPHA" IR-Fourier spectrometer "LUMOS", IR-Fourier microscope from "BRUKER", Germany), gel permeation chromatography (on liquid chromatograph with refractometric detector ("KOVO", Czech Republic), thermogravimetric analysis (on thermal analyzer "YUPITER STA" 449F3", "NETZSCH", Germany), differential thermal analysis, elemental analysis (on the device "TrusPec MICRO", "LECO"), etc.

The main provisions submitted for defense:

- synthesis and study of the structure, physicochemical properties of phenol- and monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines and amidoamines based on DNPA and polyamines (DETA, TETA, PEPA);

- effectiveness of phenol and monoalkyl(C_8-C_{12})phenol formaldehyde oligomers modified by imidazolines and amidoamines based on DNPA with polyamines (DETA, TETA, PEPA) as an inhibiting component against atmospheric corrosion, corrosion in seawater and 0.001% sulfuric acid solution in the composition of conservative fluids based on T-30 turbine oil;

- synthesis and study of the structure, physicochemical properties of monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on fatty acids obtained from various vegetable oils (sunflower, corn, palm, cottonseed, soybean) and polyamines (DETA, TETA, PEPA);

- effectiveness of anticorrosive protection of conservative fluids based on T-30 turbine oil containing monoalkyl(C_8-C_{12})phenol formaldehyde oligomers modified by imidazolines based on acids obtained from various vegetable oils (sunflower, corn, palm, cottonseed, soybean) with polyamines (DETA, TETA, PEPA under atmosphere, in seawater and 0.001% sulfuric acid solution;

- synthesis process and study of the properties of monoalkyl (C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on individual saturated and unsaturated (on the example of palmitic and oleic) acids with polyamines (DETA, TETA, PEPA);

- synthesis process and study of the properties of monoalkyl (C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on synthetic petroleum acids with polyamines (DETA, TETA, PEPA);

- effectiveness of the synthesized oligomers against atmospheric corrosion.

Scientific novelty of the work. Scientific novelty of the dissertation work consists of the development of methods for synthesis, determination and study of the scientific and theoretical foundations of the process for obtaining phenol and monoalkyl (C_8-C_{12})phenolformaldehyde oligomers enriched with polar nitrogen-containing fragments (imidazoline cycles and amine groups) mainly based on local raw materials and their use as additives in the composition of mineral oils to obtain conservative fluids:

- for the first time, phenol- and monoalkyl

(C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines and amidoamines based on DNPA and various polyamines (DETA, TETA, PEPA) were synthesized [38];

- monoalkyl (C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on fatty acids obtained from various vegetable oils (sunflower, cottonseed, palm, corn, soybean) and polyamines (DETA, TETA, PEPA) were synthesized;

- similar studies were carried out on the synthesis and study of the properties of monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on individual saturated and unsaturated carboxylic acids (on the example of palmitic and oleic acids);

- monoalkyl (C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on SPA and polyamines (DETA, TETA, PEPA) were synthesized;

- structure, physicochemical properties, molecular weight distribution were determined, thermal stability was studied in comparison with unmodified analogs and the regularities of dependences on the qualitative and quantitative composition;

- investigated the inhibitory efficiency of the synthesized oligomers in the composition of the conservative fluid based on T-30 turbine oil;

- the process flow scheme was developed combining several stages, including obtainment of fatty acids from the composition of vegetable oils, synthesis of imidazolines based on fatty acids of vegetable oils, as well as DNPA with polyamines - DETA, TETA, PEPA, the process of synthesis of monoalkyl (C_8-C_{12})phenolformaldehyde modified by imidazolines oligomers and compounding of conservative fluid.

Theoretical and practical value of the dissertation work:

- development of a method for obtaining phenol- and monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by amines containing imidazoline fragments, study of structural peculiarities, as well as thermal destruction properties of synthesized oligomers using physical research methods (IR spectroscopy, gel permeation chromatography, thermogravimetric analysis,

differential-thermal analysis, etc.);

- obtaining highly effective corrosion inhibitors mainly from local raw materials based on monoalkyl(C_8-C_{12})phenolformaldehyde oligomers enriched in polar nitrogen-containing fragments and their use in conservative fluids based on T-30 mineral oil.

- recommendations were given on the use of conservation compositions of high corrosion resistance using monoalkyl (C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on DNPA and various polyamines, as well as oligomers modified by imidazolines based on fatty acids obtained from various vegetable oils with polyamines to protect against destructive effects of corrosion of metal structures and equipment such as atmospheric corrosion, corrosion in acidic medium and seawater;

- the process flow scheme was proposed, combining several stages into one whole, including the processes of synthesis of imidazoline compounds and polycondensation of phenols (phenol-, monoalkylphenols with C_8-C_{12} alkyl substituents at the para-position) with formaldehyde in the presence of nitrogen-containing modifiers, as well as the preparation of a conservative fluid.

Publications and approbation of the dissertation work. Based on the materials of the dissertation, 39 scientific works were published, including 19 articles in domestic and foreign journals, 19 theses of reports and 1 patent of Azerbaijan Republic. Scientific articles were published in the following scientific journals: News of Azerbaijan Higher Technical Schools; Scientific Works (series of natural and medical sciences); Processes of Petrochemistry and Oil Refining; Corrosion: Materials, Protection; Plasticheskiye Massy; Sorption and Chromatography Processes; Neftepererabotka i Neftekhimiya; Mir Nefteproduktov; AutoGazoZaprovochniy Kompleks+Alternativnoye Toplivo.

The main results of the dissertation work were also reported at the international conference "Actual Problems of Chemistry and Biology" (Ganja, May 12-13, 2016), II International Turkic World Conference on Chemical Sciences and Technologies (Skopje, Macedoniya, October 26-30, 2016), Republican Scientific Conference"Macromolecular chemistry, organic synthesis and

composite materials" dedicated to the 50th anniversary of the Institute of Polymer Materials (Sumgait, October 20-21, 2016), IX Baku International Mammadaliyev Conference on Petrochemistry (Baku, October 4-5, 2016), International Scientific Conference "Actual Problems of Natural Sciences" (Ganja, May 4-5, 2017), Republican Scientific and Technical Conference dedicated to the 90th anniversary of Professor S.A. Soltanov "Fuels, Fuel Components, Special Fluids, Oils and Additives" (Baku, October 3, 2017), International Scientific and Technical Conference "Petrochemical Synthesis and Catalysis in Complex Condensed Systems" dedicated to the 100th anniversary of academician B.K. Zeynalov (Baku, June 29-30, 2017), 6th Rostocker International Conference: "Thermo-physical Properties for Technical Thermodynamics" (Rostock, Germany, July 17-18, 2017), International Scientific Conference "Functional Monomers and Polymeric Materials with Special Properties" (Sumgait, October 15-16, 2017), 9th International Symposium "Molecular Mobility and Order in Polymer Systems" (St. Petersburg, Peterhof, June 19-23, 2017), International Scientific-Practical Conference "Innovative Prospects for the Development of Oil Refining and Petrochemistry" dedicated to the 110th anniversary of Academician V.S. Aliyev (Baku, October 9-10, 2018), Scientific Conference dedicated to the 110th anniversary of Academician M. Nagiyev (Baku, 2018), XXI Mendeleev Congress on General and Applied Chemistry (Saint Petersburg, September 9-13, 2019), International Scientific Conference "Actual Problems of Modern Chemistry" dedicated to the 90th anniversary of Y.H.Mammadaliyev Institute of Petrochemical Processes (Baku, October 2-4, 2019), 9th Rostocker International Conference: "Thermo-physical Properties for Technical Thermodynamics" (Rostock, Germany, October 15, 2020), Republican Scientific Conference "Modern Problems of Chemistry" (Sumgait, April 15-16, 2021)

The organization where the dissertation work was carried out. The dissertation work was carried out at academician Y.H.Mammadaliyev Institute of Petrochemical Processes of National Academy of Sciences of Azerbaijan in accordance with the work

program 17/2009, 17/2017, under registration number 0109AZ2003.

The scope of the dissertation work. The dissertation work consists of an introduction, 9 chapters, conclusions, a reference list, annexes, including 111 figures, 66 tables and technological scheme. The dissertation work excluding figures, tables, reference list of 303 titles and annexes consists of 333853 characters (including introduction 18554, first chapter 99426, second chapter 15326, third chapter 26227, fourth chapter 19562, fifth chapter 24386, sixth chapter 87289, seventh chapter 22759, eighth chapter 10593, ninth chapter 4853 and outputs 4878 characters).

Introduction substantiates the relevance of the chosen topic, the aim of the dissertation work, scientific novelty, practical value, and reliability of the results. The essence of the dissertation chapters, approbation, structure, volume and publications corresponding to the work are briefly described.

The first chapter deals with a broad review of contemporary literature on high-molecular compounds used as corrosion inhibitors, phenol-formaldehyde resins were characterized, methods of their modification, scope of application, various additives of an alkyl phenol base were studied, assessment of the change in composition and properties, fuels and oils used with their use was given, allowing to assess the advantages and disadvantages of their use. Water and oil-soluble nitrogen-containing corrosion inhibitors were also studied, effect of their protective mechanism was studied on various metals, alloys as a result of CO_2, H_2S corrosion, corrosion in the medium of various electrolytes and atmospheric medium.

The second chapter presents preparation and characterization of the starting compounds, methodology of the analyzes carried out, methodology for the study of conservative fluids.

The third chapter is devoted to the synthesis of imidazolines based on DNPA with polyamines (DETA, TETA, PEPA), the development of a method for modifying phenolformaldehyde oligomers with imidazolines of various compositions. The structure of the synthesized imidazolines and phenolformaldehyde oligomers modified by them was studied. Molecular weight distribution, thermal stability and anticorrosive efficiency of the synthesized

oligomers were studied in the composition of mineral oil T-30 separately and in the composition with the products of nitration of $C_{14}C_{28}$ olefins in atmospheric medium, seawater and 0.001% aqueous solution of sulfuric acid.

The fourth chapter is devoted to the synthesis of monoalkyl (C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on DNPA and polyamines of various compositions (DETA, TETA, PEPA). The structure of monoalkyl(C_8-C_{12})phenol formaldehyde oligomers modified by imidazolines, their thermal stability and anticorrosive efficiency in the composition of T-30 mineral oil were studied separately and in a composition with nitration products of $C_{14}H_{28}$ olefins in atmospheric medium, seawater and 0.001% aqueous solution of sulfuric acid.

The fifth chapter is devoted to the synthesis of amidoamines based on DNPA with polyamines (DETA, TETA, PEPA), and modification process of monoalkyl(C_8-C_{12})phenolformaldehyde oligomers with amidoamines of the composition. The structure of the synthesized amidoamines and monoalkyl(C_8-C_{12})phenol phormaldehyde oligomers modified by them was studied. Molecular weight distribution, thermal stability and anticorrosive efficiency of the synthesized oligomers in the composition of conservative fluids based on mineral oil T-30 were studied in three media (atmospheric, seawater, 0.001% aqueous solution of sulfuric acid).

The sixth chapter is devoted to obtainment of fatty acids from various vegetable oils (sunflower, corn, palm, cottonseed, soybean), synthesis of imidazolines based on them with various polyamines (DETA, TETA, PEPA) and modification of monoalkyl(C_8-C_{12}) phenolformaldehyde oligomers with imidazolines of the composition. Structure of fatty acids, imidazolines synthesized on their basis, and monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by them were studied. Molecular weight distribution, thermal stability and anticorrosive efficiency of the synthesized oligomers in the composition of T-30 mineral oil were studied in three media (atmospheric, seawater, 0.001% aqueous solution of sulfuric acid).

The seventh chapter presents physicochemical parameters of

monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on individual carboxylic acids (saturated by palmitic and unsaturated - oleic) with polyamines (DETA, TETA, PEPA), studied the structure of imidazolines synthesized on their basis monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by them. Anticorrosive efficiency of the synthesized oligomers was studied in the composition of conservative fluids based on mineral oil T-30 in atmospheric medium.

The eighth chapter presents the method for obtaining, structure, physicochemical parameters of SPA obtained on their basis with polyamines (DETA, TETA, PEPA) of imidazolines and monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines of the composition. Anticorrosive efficiency of the synthesized oligomers was studied in the composition of conservative fluids based on mineral oil T-30 in atmospheric medium.

The ninth chapter presents a process flow scheme, including the stages of obtaining nitrogen-containing components, synthesis process of oligomers modified by them, and compounding of turbine oil T-30 with monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines of various compositions.

Personal participation of the author. The main ideas included in the dissertation work, problem statement, the directions of the research, conducting experimental experiments were carried out directly by the author.

THE MAIN CONTENT OF THE WORK

Development of new methods for modification of PhFO doesn't lose its relevance, which is associated with their high reactivity, the presence of real raw materials (oil, gas, coal, etc.). Due to the protective properties, anticorrosive additives occupy an important place among the areas of application of compounds based on PhFO. Simultaneously, modification by nitrogen-containing compounds for the purpose of obtaining materials with a set of

required properties is of particular importance. Adding of nitrogen-containing functional groups into the composition of PhFO macromolecules contributes to the enrichment of the latter with polar fragments along with methylol and hydroxyl groups, which in turn improves adhesion to a metal surface, the crystal structure of which has a sufficiently high polarity and enhances the protective effect using conservative fluids. Carrying out such studies in Azerbaijan - country rich in oil resources, is of great importance both from a theoretical and practical point of view.

1. Synthesis and study of the properties of phenol- and monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines and amidoamines based on DNPA and polyamines - DETA, TETA, PEPA

Baku oils are distinguished by the presence of a large amount of natural petroleum acids, such as monocyclic, bicyclic and polycyclic naphthenic, as well as aliphatic and aromatic acids. Their amount ranges from 0.1-2% for the oils from various Baku wells. DNPA is obtained with a hydrocarbon content of less than 2.5%, where mass fraction of petroleum acids is> 98.8%, mass fraction of mineral oils is <1.7%, acid number is ~ 265 mgKOH/g, density is 0.960 g/cm3, etc. using advanced technologies at Heydar Aliyev Baku Oil Refinery. For the purpose of obtaining imidazolines and amidoamines of various compositions based on DNPA, they were reacted with PEPA (average molecular weight ~220, boiling point > 268°C at atmospheric pressure, density 0.990 g / cm3, nitrogen content 33.7%), as well as with their low-boiling fractions - DETA (average molecular weight ~ 103, boiling point> 206.7°C at atm. pressure, density 0.952 g/cm3, nitrogen content 40.6%) and TETA (average molecular weight ~ 146, boiling point> 276.5°C at atm. pressure, density 0.981 g/cm3, nitrogen content 36%).

Synthesis of imidazolines was carried out at 1-3:1 molar ratio of DNPA to DETA, TETA and PEPA respectively, at a temperature 230-240°C 3-3.5 hours to obtain imidazolines. When choosing molar ratios, special attention is paid to the amount of free amine fragments in the composition of the final products, determining the

functionality of the latter. The indicated molar ratios contribute to the partial consumption of amine fragments for the formation of imidazoline ring. Synthesized nitrogen-containing compounds are viscous products.

The process for obtaining PhFO and APhFO modified by imidazolines based on DNPA and polyamines was studied. The synthesis was carried out by the interaction of phenol with formaldehyde at a molar ratio of 1:0.85 in an acidic medium at 95-98°C until the appearance of turbidity, indicating the formation of condensation centers (~ 30-40 minutes) and followed by the addition of imidazolines in portions at a low temperature (~50°C) and raising the temperature up to 95-98°C, at which the process was carried out for another 45-120 min. until obtaining resin.

At the initial stage, the syntheses were carried out in several directions to achieve good solubility of oligomers in non-polar solvents (benzene, toluene, solvent), as well as in oils:

- partial substitution of phenol by monoalkyl(C_8-C_{12})phenols;
- synthesis of oligomers based on monoalkyl(C_8-C_{12})phenols;
- carrying out the modification of PhFO in a solvent medium - dioxane;
- recondensation of the modified PhFO in a solvent medium;
- by butoxylation in an acidic medium of PhFO recondensed in a solvent.

The next studies were mainly carried out on the basis of monoalkyl(C_8-C_{12})phenols according to the data obtained by the tests.

The structures of PhFO and APhFO modified by imidazolines based on DNPA and PA was determined using IR-Fourier spectrometer in the wavelength range of 600-4000 cm^{-1} in comparison with the initial components. Comparative data of spectral analyzes were presented on the example of PhFO modified by imidazoline based on DNPA and DETA. The IR-spectrum of DNPA (fig. 1) revealed absorption bands corresponding to deformation at 1454 cm^{-1}, stretching at 2922 cm^{-1} vibrations of C-H bonds of CH_2 groups, deformation vibrations 1377 cm^{-1}, stretching vibrations 2860 cm^{-1} bonds of CH_3 groups, deformation 1414 cm^{-1} vibrations of C-H

bonds of CH_2 groups in the α-position to COOH groups, stretching vibrations 1227, 1289 cm^{-1} C-O bonds of COOH groups, stretching vibrations 1704 cm^{-1} C=O groups and bending vibration of 935 cm^{-1} O-H bonds.

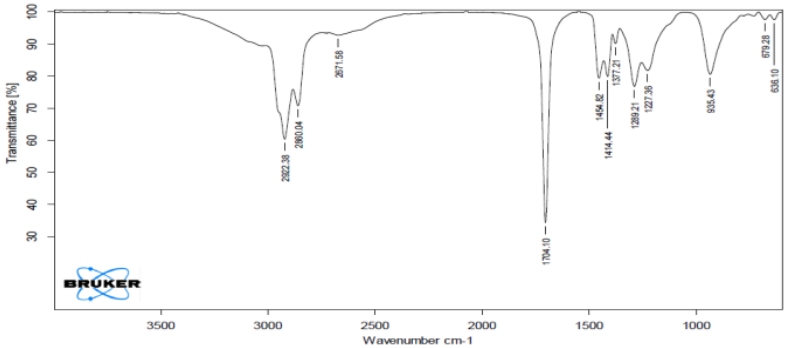


Figure 1. IR-spectrum of DNPA

The IR-spectrum of DETA (fig. 2) presents absorption bands of pendulum vibrations 766 cm^{-1} of C-H bonds of CH_2 groups, deformation 1452 cm^{-1}, stretching 2828 cm^{-1} vibrations of C-H bonds of CH_2 groups, deformation vibrations 1347 cm^{-1} , stretching 2807cm^{-1} vibrations of C-H bonds of CH_3 groups, deformation 1596 cm^{-1}, stretching 3277, 3353 cm^{-1} vibrations of N-H bonds, stretching 1065, 1128, 1300 cm^{-1} vibrations of C-N bonds.

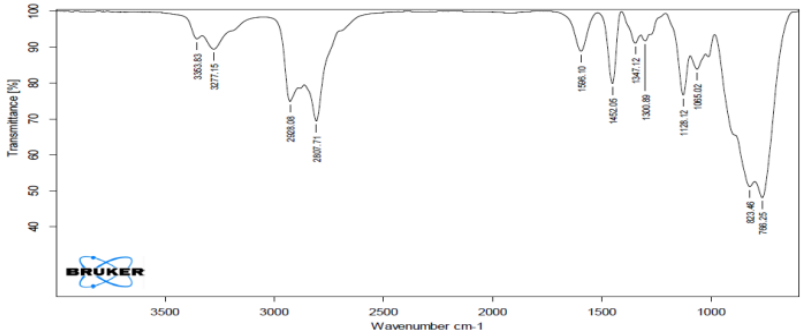


Figure 2. IR spectrum of DETA

IR-spectrum of imidazoline based on DNPA and DETA (fig. 3) showed absorption bands corresponding to pendulum 725

cm^{-1} vibrations of C-H bonds of CH_2 groups, deformation vibrations of 1453 cm^{-1} and stretching 2922 cm^{-1} vibrations of C-H bonds of CH_2 groups, deformation 1373 cm^{-1}, stretching 2858 cm^{-1} vibrations of C-H bonds of CH_3 groups, deformation 1547 cm^{-1} and stretching vibrations 3291 cm^{-1} vibrations of N-H bonds, stretching 1010, 1144, 1266 cm^{-1} vibrations of C-N bonds, stretching 1644 cm^{-1} vibrations of C=N bonds. Presumably, vibrations of N-H bonds of amide groups were assigned at 3065 cm^{-1}.

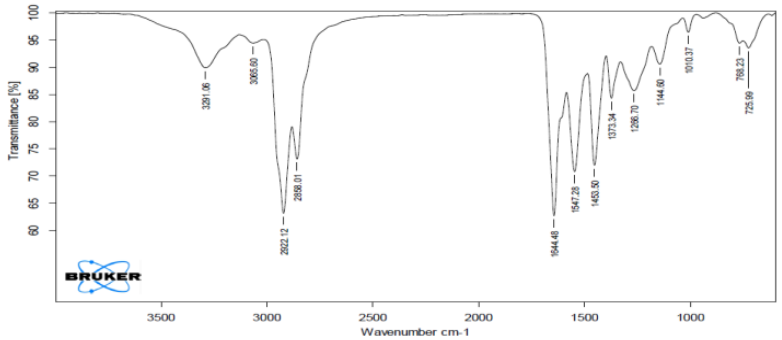


Figure 3. IR-spectrum of imidazoline based on DPNA:DETA in a molar ratio of 1:1

IR-spectrum of PhFO modified by imidazoline based on DPNA and DETA exhibits the following absorption bands: stretching vibrations of 3297 cm^{-1} N-H bonds, stretching vibrations of 3022 cm^{-1} C-H bonds of phenol nucleus, stretching vibrations of 2923 cm^{-1} C-H bonds CH_2 groups, stretching vibrations 2853 cm^{-1} C-H bonds of CH_3 group, bending vibrations 1598 cm^{-1} C-H bonds of the phenol nucleus, vibrations - CH_2-NH-CH_2 - bonds of the secondary amine -1505 cm^{-1}, deformation vibrations 1445 cm^{-1} C-H bonds CH_2, deformation vibrations 1366 cm^{-1} C-H bonds CH_3, stretching vibrations 1174, 1227 cm^{-1} C-N bonds, stretching vibrations 1103 cm^{-1} C-O bonds of phenolic C-OH groups, stretching 1015 cm^{-1} vibrations of C-O bonds C-OH groups of primary alcohols, deformation 752, 817, 888 cm-1 vibrations C-H bonds of the substituted benzene ring, pendulum vibrations of CH bonds of CH_2 groups at 689 cm^{-1}.

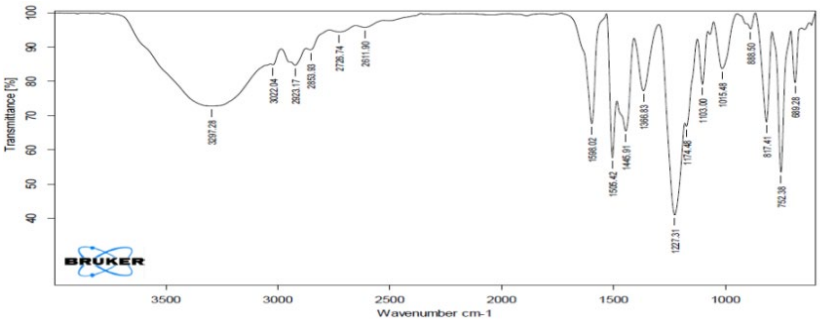


Figure 4. IR spectrum of PhFO modified by imidazoline based on DNPA:DETA obtained in a molar ratio of 1:1

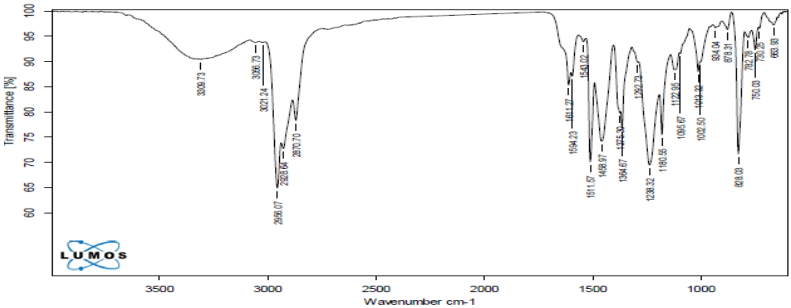


Figure 5. IR-spectrum of APhFO modified by imidazoline based on DNPA:DETA obtained in a molar ratio of 1:1

In the spectrum of APhFO modified by imidazolines based on DNPA and DETA (fig. 5), the following absorption bands were assigned corresponding to the deformation vibrations of the C–H bonds of the benzene ring at 663, 750, 782, 828, 878 cm^{-1}, and deformation vibrations of O–H group of the acid at 934 cm^{-1}, stretching vibrations of C-O bonds of primary alcohol 1095 cm^{-1}, vibrations of C-N groups 1122, 1238 cm^{-1}, vibrations of C-O bonds of phenol at 1180 cm^{-1}, stretching vibrations of C-H groups 1292 cm^{-1}, deformation vibrations 1364, 1375 cm^{-1} and stretching vibrations 2870 cm^{-1} of C-H bonds of CH_3 groups, deformation vibrations 1458 cm^{-1} and stretching vibrations of 2928, 2956 cm^{-1} of C-H bonds of CH_2 groups, deformation vibrations of N-H bonds of 1511 cm^{-1}, deformation vibrations of C-H bonds of phenol nucleus 1543, 1594 cm^{-1}, vibrations of 1611 cm^{-1} of C=N bonds, stretching

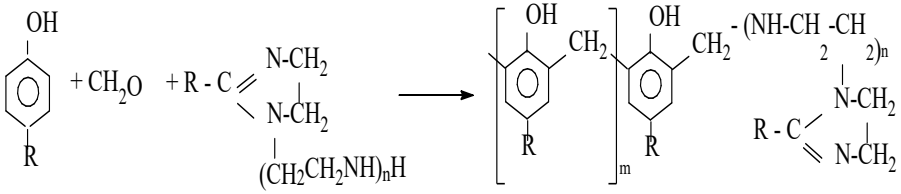
vibrations of phenolic OH bonds at 3309 cm^{-1}.

Similarly, IR-spectra of phenolic oligomers modified by imidazolines, were recorded and decoded of various qualitative and quantitative compositions in comparison with the initial components, their images were given in 3d format. As a result of the analysis of IR spectra, both the preparation of imidazolines and the process of modification were confirmed. Summarizing the data, we can conclude: disappearance of absorption bands of acid fragments at 1704 cm-1 corresponding to C=O groups, appearance of absorption bands at ~ 1644 cm-1 corresponding to the vibrations of C=N bonds confirms the preparation of imidazolines. Spectra of the final products assigns both absorption bands characteristic for imidazoline (C=N, N-H, C-N and other bonds) and for phenolic oligomeric structure (Ar-C, Ar-C-Ar, alcohol and phenolic C-OH, C-C (ar), etc.) with small offsets.

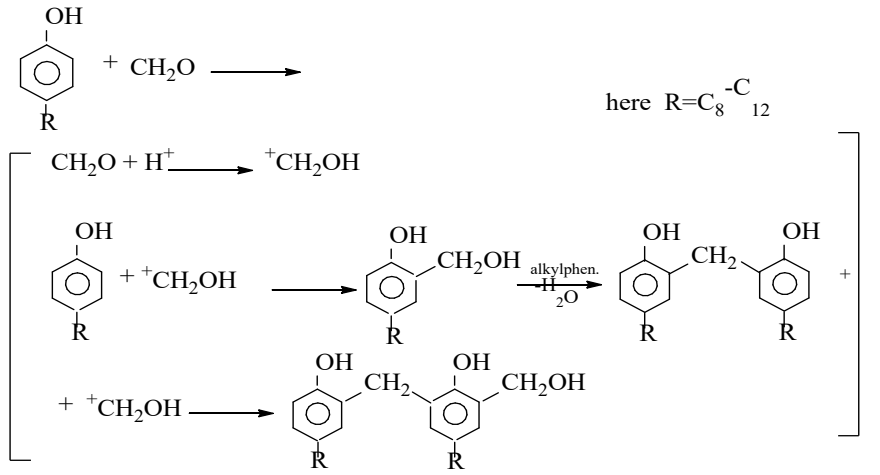
It should be noted that synthesis of PhFO and APhFO in an acidic medium causes the chain growth in ortho-position to phenolic hydroxyl with the formation of methylene bridges between phenolic nuclei, and the modifier is added to the reaction medium later, after the beginning of the formation of the oligomeric chain. Consequently, a high probability of the latter being attached to the end of the chain is inevitable. But it doesn't exclude possibility of attaching the modifier to the middle of the oligomeric chain, so that polyfunctionality of imidazolines and amidoamines allows the chain to grow in two or more directions.

As is evident from the above scheme obtaining oligomers modified by imidazolines of different composition can be presented as follows:

Obtaining APhFO modified by imidazoline based on DNPA and PA. Scheme 1.



n=1-6 depending on selection of PA



Physico-chemical properties of both PhFO (tab. 1) and APhFO (tab. 2) modified by imidazolines of various compositions were determined. Unlimited solubility of APFO in non-polar solvents, including mineral oils, was revealed; therefore, further researches in this direction were most expedient.

Study of the molecular weight distribution (MWD) of PhFOs modified by imidazolines based on DNPA and polyamines was carried out on a high-performance liquid chromatograph manufactured by "KOVO" (Czech Republic) equipped with a refractometric detector by size exclusion chromatography. "Separon SGX" stationary phase was used; dimethylformamide was taken as an eluent with a flow rate of 0.3 ml / min. Analyzes were carried out at a temperature of 20-25°C. Calculations were carried out according to the equations:

$$Mw = \Sigma Mi\omega i$$

$$Mn = 1/\omega i/\Sigma Mi$$

where Mi – is the molecular weight corresponding to the i area of the chromatogram, ωi is the fraction of the area of part i.

Table 1.

Physico-chemical properties of PhFO, modified by imidazolines of various compositions

№	Qualitative and quantitative composition of imidazoline (number of moles per 1 mol of phenol)	Appearance	Density kg/m^3	Ubbelohde drop point, ^{0}C	Freezing point, ^{0}C	Non-volatile compounds, %	Solubility properties				
							Benzene	Dioxane	Acetone	Ethanol	Turbine oil T-30
1	2	3	4	5	6	7	8	9	10	11	12
1	DNPA:DETA 1:1 /0.05/	Brown-colored low plast. resinous mass	1180	73,5	-	92,3	-	+	+	+	±
2	DNPA:DETA 1:1 /0.05/	Brown-colored plastic mass	1200	54	-	88,4	-	±	+	+	±
3	DNPA:DETA 1:1 /0.05/	Light-brown colored viscous resin	-	-	-	-	-	+	+	+	±
4	DNPA:DETA 1:1 /0.1/	Brown-colored hard resin	1130	62	-	78,6	-	+	+	+	±
5	Mod. of the mix. of phenol and alkylpenol DNPA:DETA 1:1 /0.05/	Dark-brown fluid	1044	-	+14	77,8	+	+	+	+	±
6	Modification in a solvent medium (dioxane) DNPA:DETA 1:1	Dark brown fluid mass	1130	-	-10	63,0	-	+	+	+	±

Continuation

1	2	3	4	5	6	7	8	9	10	11	12
7	Modification in a solvent medium DNPA:DETA 1:1	Fluid at a room temperature	1160	-	+5	72,3	-	+	+	+	±
8	DNPA:TETA 2:1 /0.015/	Brown colored fluid mass	1170	-	+15	80,4	-	±	+	+	±
9	DNPA:TETA 2:1 /0.03/	Brown-colored resinous mass	1160	47-57	-	81,8	-	+	+	+	±
10	DNPA:TETA 2:1 /0.06/	Brown-colored resinous mass	1140	54-58		81,0	-	+	+	+	±
11	DNPA:PEPA 3:1 /0.01/	Brown-colored plastic mass	1140	45-50	-	86,1	-	+	+	+	
12	DNPA:PEPA 3:1 /0.02/	Brown colored low plastic mass	1160	53-55	-	83,0	-	-	+	+	±
13	Monoalkyl (C_8-C_{12}) PhFO DNPA:DETA 1:1 /0.1/	Plast., but fluid at room temperature, light-brown colored mass	1010	-	+18	88,0	+	+	+	+	±
14	Recondensation in a solvent (dioxane) and butoxylation DNPA:DETA 1:1	Dark-brown colored fluid mass	920	-	-	67,4	-	+	+	+	±

Note: (+) – well-soluble, (±) – partially soluble, (-) – insoluble

Table 2.

Physico-chemical properties of APhFO, modified by imidazolines of various compositions

№	Qualitative and quantitative composition of imidazoline (number of moles per 1 mol of phenol)	Appearance	Density, kg/m^3	Ubbelohde drop point, ^{0}C	Freezing point, ^{0}C	Non-volatile compounds %	Solubility properties					
							Benzene	Acetone	Ethanol	DMFA	Gasoline	Turbine oil T-30
1	DNPA:DETA 1:1 /0.1/	Dark-brown resinous mass	981	35	-	95.72	+	+	+	+	+	+
2	DNPA:DETA 1:1 /0.2/	Light-brown resinous mass	955	40	-	88.07	+	+	±	±	+	+
3	DNPA:DETA 1:1 /0.3/		955	42	-	85.54	+	+	±	±	+	+
4	DNPA:TETA 2:1 /0.1/	Dark-brown resinous mass	992	Fluid at room temp.	-	91.21	+	+	+	+	+	+
5	DNPA:TETA 2:1 /0.2/		975	37	-	90.46	+	+	+	+	+	+
6	DNPA:PEPA 1:1 /0.05/		953	Fluid at room temp.	3	82.48	+	+	+	+	+	+
7	DNPA:PEPA 1:1 /0.1/		951	35.5	-	90.45	+	+	+	+	+	+
8	DNPA:PEPA 1:1 /0.2/		976	36.5	-	83.81	+	+	+	+	+	+
9	DNPA:PEPA 3:1 /0.1/	Light-brown resinous mass	1054	47	-	93.25	+	+	+	+	+	+

Note: (+) – well-soluble, (±) – partially-soluble, (-) – insoluble

The weight average Mw and number average Mn molecular weights of these products were calculated according to the chromatograms. The properties are set into table 3.

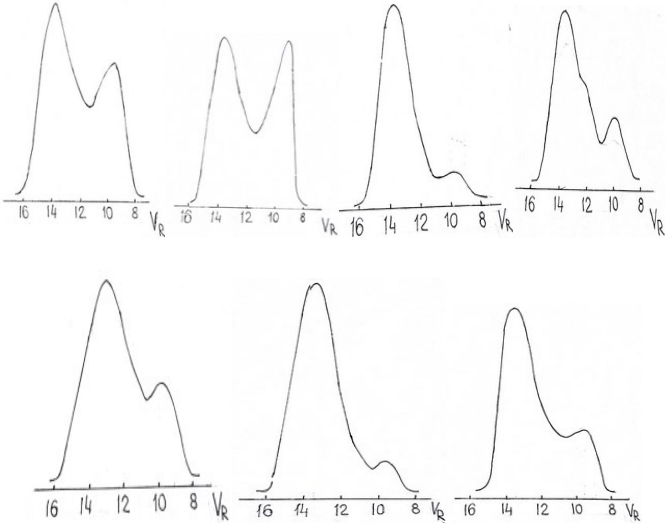


Figure 6. Gel chromatograms of imidazolines modified on the basis of DNPA and PA of different compositions of PhFO

Table 3.

Molecular weight distribution of PhFO, modified by imidazolines of different compositions

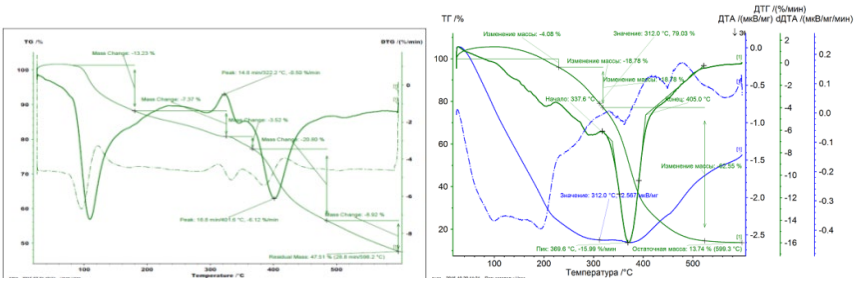
№	Samples of modified PhFO	Fractional compos., %	Molecular weight distribution		
			Mw	Mn	Mw/Mn
1	2	3	4	5	6
1	PhFO modified by imida-zolines based on DNPA and DETA (1:1), in an amount of 0.05 mol per 1 mol phenol	33.5 66.5 -	5300 780 2305	4340 475 668	1.22 1.64 3.45
2	PhFO obtained similarly to sample 1 by contin. of the process in 2 times longer	43.5 56.5 -	5354 670 2757	4260 470 780	1,25 1.42 3.53
3	PhFO, obtained similarly to sample 1 with 50% substitution of phenol by alkylphenols	86.0 14.0 -	4943 617 990	4268 435 470	1.16 1.42 2.11

Continuation

1	2	3	4	5	6
4	PhFO modified by imidazolines based on DNPA and DETA in solvent dioxane	15.0 85.0	4580 783 1363	4098 550 630	1.12 1.42 2.16
5	PhFO, modified similarly to sample 4 in half the amount of a modifier	23.0 87.0 -	5250 790 1868	4456 522 665	1.12 1.50 2.81
6	PhFO modified imidazolines based on DNPA and TETA (2:1), in the amount of 0.015 mol per 1 mol phenol	8.5 91.5 -	5020 704 1058	4550 446 480	1.10 1.58 2.20
7	PhFO modified by imidazolines based on DNPA and PEPA (3:1), in the amount of 0.01 mol per 1 mol phenol	18.0 82.0 -	5194 870 1636	4643 562 658	1.12 1.55 2.49

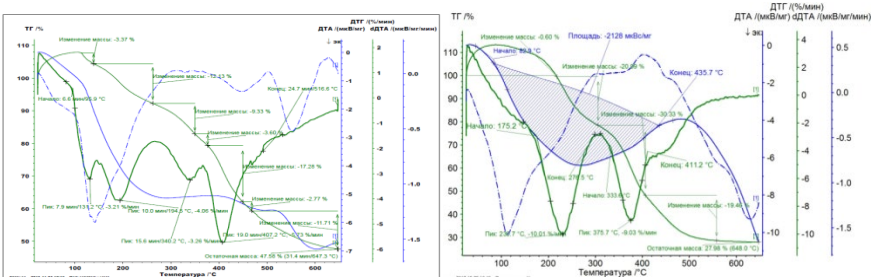
As is evident from the data in table 3, PhFOs modified by imidazolines of various compositions consist of two fractions - high molecular weight and low molecular weight. In PhFOs modified by low molecular weight imidazolines (DNPA with DETA), the percentage of the high molecular weight fraction is higher. Separate fractions of oligomers modified by imidazolines of various compositions are characterized by narrower, and the final products by wider polydispersity. Based on the analysis of the data, it can be assumed that the number of repeating phenol- and alkylphenolformaldehyde fragments varies in the range of 20-35 in the high-molecular fraction, and 3-7 in the low-molecular fraction.

Thermal stability of PhFO and APhFO modified by imidazolines based on DPNA and polyamines of various compositions was determined by thermogravimetric method (TGA) in comparison with unmodified oligomers. The studies were carried out on thermal analyzer “YUPİTER STA 449 F3” (company NETZSCH, Germany) in an inert atmosphere (nitrogen) at a temperature range of 25-650°C with a heating rate of 10 K/min. The dependence of heat resistance on the composition of oligomers was studied. Figures 7-8 presents the samples of TGA curves.



a b

Figure 7. TGA curves of unmodified a-PhFO and b-APhFO



a b

Figure 8. TGA curves a-PhFO, modified by imidazoline based on DNPA and DETA, b – APHFO, modified by imidazoline based on DNPA and DETA

Table 4.

Dependence of the residual mass of samples on temperature

№	Imidazoline composition used in APhFO modification	Residual mass,%, at temperature, ^{0}C					
		100	200	300	400	500	600
1	Unmodified APhFO	105	100	81.6	32.5	15	13.74
2	DNPA:DETA=1:1	113	104.5	78.75	51.2	31	27.98
3	DNPA:TETA=2:1	134	126	96	75.5	62.5	60.80
4	DNPA:PEPA=3:1	116	110	86	47	29	-

Analysis of the data showed that, as a result of modification of PhFO and APhFO by imidazolines of various compositions, thermal stability is significantly higher (there is a sample with a residual mass index of 60.8% at 650°C) in comparison with unmodified oligomers,

but regularity isn't observed according to the structure. Thermal destruction of all samples begins mainly at 300°C, it reaches a more noticeable line at 400°C, goes even deeper at 500°C and remains stable up to 650°C. The mass loss is accompanied by endo-effects proving the degradation process, and it is mainly observed above 200°C.

The study of the anticorrosive resistance of phenol- and monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on DNPA and polyamines in turbine oil T-30 was carried out according to ГОСТ 9.054-75 (conservative oils, lubricants and inhibited film-forming petroleum compositions) using "St-3", "St-10" metal plates in the hydrochamber G-4, 08Ю plates in the climatic chamber "Corrosion Box 1000E", seawater and 0.001% aqueous solution of H_2SO_4 until the first corrosion foci appears. Due to the limited solubility of PhFOs modified by imidazolines of various compositions and taking into account the positive effect on the anticorrosive effect of the nitration products of $C_{14}H_{28}$ α-olefins, it was advisable to study the synthesized compounds also in a composition with the latter. The results are set into table 5 and 6.

Table 5.

Determination of the duration of anti-corrosion protection of conservative fluids based on turbine oil T-30 and PhFO modified by imidazolines based on DNPA and PA

№	Conservative fluid composition	Content in oil, %	Г- 4, days	Seawater, days	0.001% aq.sol. H_2SO_4, days
1	2	3	4	5	6
1	T-30	100	34	15	9
2	T-30 PhFO+APFO mod.imidaz. DNPA:DETA=1:1 Nitrocompoud of $C_{14}H_{28}$ olefins	95 2.5 2.5	217	120	126
3	T-30 PhFO mod. by imidaz. DNPA:DETA= 1:1	95 5	383	179	194

Continuation

1	2	3	4	5	6
4	T-30 PhFO+APhFO mod. by imidaz. DNPA:TETA= 2:1 Nitrocompound of $C_{14}H_{28}$ olefins	95 2.5 2.5	397	301	276
5	T-30 PFhO mod. by imidaz. DNPA:TETA= 2:1	95 5	196	114	138
6	T-30 PhFO mod.by imidaz. DNPA:PEPA= 3:1	95 5	214	135	152
7	T-30 PhFO+APhFO mod. by imidaz. DNPA: DETA= 1:1 Nitrocompound of $C_{14}H_{28}$ olefins	90 5 5	247	150	150
8	T-30 PhFO mod.by imidaz. DPNA: DETA= 1:1	90 10	457	205	230
9	T-30 PhFO+APhFO mod.by imidaz. DPNA:TETA= 2:1 Nitrocompound of $C_{14}H_{28}$ olefins	90 5 5	465	368	300
10	T-30 PhFO mod. by imidaz. DPNA:TETA= 2:1	90 10	230	187	200
11	T-30 PhFO mod.by imidaz. DNPA:PEPA= 3:1	90 10	240	195	207

Table 6.

Determination of the duration of anticorrosive protection of conservative fluids based on turbine oil T-30 and APhFO modified by imidazolines based on DPNA and PA

№	Conservative fluid composition	Content in oil, %	«Corrosion Box 1000E» condensation mode, days	Sea-water, days	0.001% aq. sol. H_2SO_4, days
1	2	3	4	5	6
1	T-30	100	34	15	9
2	T-30 APHFO mod.by imidaz. DNPA:DETA=1:1	95 5	152	57	98
3	T-30 APHFO mod.by imidaz. DNPA:DETA=1:1	90 10	172	109	121
4	T-30 APHFO mod. by imidaz. DNPA:DETA=1:1	95 5	177	72	112
5	T-30 APHFO mod.by imidaz. DNPA:DETA=1:1	90 10	183	112	135
6	T-30 APHFO mod.by imidaz. DNPA:DETA=1:1	95 5	179	88	124
7	T-30 APHFO mod.by imidaz. DNPA:DETA=1:1	90 10	188	121	147
8	T-30 APHFO mod.by imidaz. DNPA:TETA=2:1	95 5	188	116	129
9	T-30 APHFO mod.by imidaz. DNPA:TETA=2:1	90 10	204	122	131
10	T-30 APHFO mod.by imidaz. DNPA:TETA=2:1	95 5	226	139	163
11	T-30 APHFO mod. by imidaz. DNPA:TETA=2:1	90 10	245	146	170

Continuation

1	2	3	4	5	6
12	T-30 APHFO mod.by imidaz. DNPA:PEPA=1:1	95 5	205	105	119
13	T-30 APHFO mod.by imidaz. DNPA:PEPA=1:1	90 10	211	114	124
14	T-30 APHFO mod. by imidaz. DNPA:PEPA=1:1	95 5	208	111	126
15	T-30 APHFO mod.by imidaz. DNPA:PEPA=1:1	90 10	214	119	133
16	T-30 APHFO mod.by imidaz. DNPA:PEPA=1:1	95 5	212	118	131
17	T-30 APHFO mod.by imidaz. DNPA:PEPA=1:1	90 10	220	126	139
18	T-30 APHFO mod. by imidaz. DNPA:PEPA=3:1	95 5	230	134	144
19	T-30 APHFO mod.by imidaz. DNPA:PEPA=3:1	90 10	240	141	157
20	T-30 + APHFO mod.by imidaz. DNPA:DETA=1:1 Nitrocompound of $C_{14}H_{28}$ olefins	90 5 5	220	184	198
21	T-30 + APHFO mod.by imidaz. DNPA:TETA=2:1 Nitrocompound of $C_{14}H_{28}$ olefins	90 5 5	310	241	270
22	T-30 + APHFO mod. by imidaz. DNPA:PEPA=3:1 Nitrocompound of $C_{14}H_{28}$ olefins	90 5 5	253	156	185

Based on the properties presented in table 5 and 6, we can say that:
- conservative fluids containing oligomers modified by imidazolines based on DNPA and PA of various compositions are much superior to the parameters of the base;
- PhFO and APhFO containing conservative liquids, modified by imidazolines based on DNPA and PA of various compositions exhibit a high protective effect as corrosion inhibitors in comparison with unmodified compositions with the only drawback - limited solubility of PhFO in oil;
- increase in the oligomer content of oil leads to increase in anti-corrosion protection indicators regardless of the research environment;
- the use of modified PHFOs in the composition of the nitrocompound of $C_{14}H_{28}$ α-olefins has a positive effect on inhibiting properties and solubility;
- modified imidazoline based on DNPA:TETA = 2:1 /phenol + monoalkyl(C_8-C_{12})phenol/formaldehyde oligomer possess the best anticorrosive protection in a composition with the product of nitration of $C_{14}H_{28}$ α-olefins. The first corrosion foci was observed in the hydrochamber after 465 days, in seawater after 368 days, in 0.001% H_2SO_4 solution after 300 days.
- the best result of the inhibitory action among alkylphenol oligomers belongs to monoalkyl(C_8-C_{12})PhFO, modified by imidazoline based on DNPA and TETA in 2:1 molar ratio that causes appearance of the first corrosion foci in conservative fluid in climatic hydrochamber after 245 days, in seawater after 146 days, in 0.001% aqueous solution of H2SO4 after 170 days. Similar indicators are, correspondingly, in a hydrochamber after 310 days, in seawater after 241 days, in 0.001% H_2SO_4 solution after 270 days by the use of it in a composition with a nitration product of $C_{14}H_{28}$ α-olefins.

2. Synthesis and study of the properties of monolkyl (C_8-C_{12})phenolformaldehyde oligomers, modified by amidoamines based on distilled natural petroleum acids and polyamines

Synthesis of amidoamines was carried out similarly to

obtaining imidazolines, but at 130-140°C and a molar ratio of acid:PA of 3:1 in the case of using DETA, 1-4:1 in the case of using TETA and 1-5:1 in the case of using PEPA. The choice of molar ratios of the initial components provides for a partial consumption of amine hydrogen atoms, since the presence of the latter in the composition of the final products was needed for the modification process with their use. The duration of the process was ~ 3-3.5 h. Synthesis of APhFOs modified by amidoamines was carried out similarly to the method described in the previous section.

The results of the studies to determine physicochemical properties of APhFOs modified by amidoamines of various compositions showed that oligomers dissolve indefinitely in polar and non-polar solvents. Elemental compositions of some samples of the synthesized oligomers were determined on LECO TrusPeco instrument. The results were set into the table 7.

Table 7.

Elemental composition of APhFO modified by amidoamines

№	Oligomer composition	Elements, %		
		C	H	N+O
1	APhFO modified by amidoamines based on DNPA:DETA, obtained in a molar ratio of 3:1	79.9	9.13	10.97
2	APhFO modified by amidoamines based on DNPA:TETA, obtained in a molar ratio of 3:1	77.68	9.20	13.12
3	APhFO modified by amidoamine based on DNPA:PEPA obtained in a molar ratio of 1:1	71.52	9.38	19.1
4	APhFO modified by amidoamine based on DNPA:PEPA obtained in a molar ratio of 3:1	69.4	9.01	21.59
5	APhFO, modified by amidoamine based on DNPA:PEPA obtained in a molar ratio of 5:1	72.4	9.10	18.5

The structure of APhFOs modified by amidoamines based on

distilled natural petroleum acids and polyamines was determined. IR spectroscopic analysis was carried out for a more detailed study of the final products using IR Fourier microscope. Therefore, 5 points were selected on the image of the APhFO sample surface modified by amidoamine based on DNPA and PEPA in a molar ratio of 1:1, and the IR spectra were recorded.

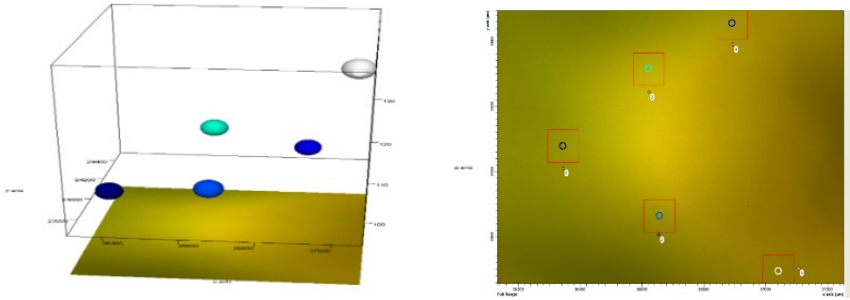


Figure 9. 3d-image of the APhFO surface modified by amidoamine based on DNPA and PEPA in a molar ratio of 1:1

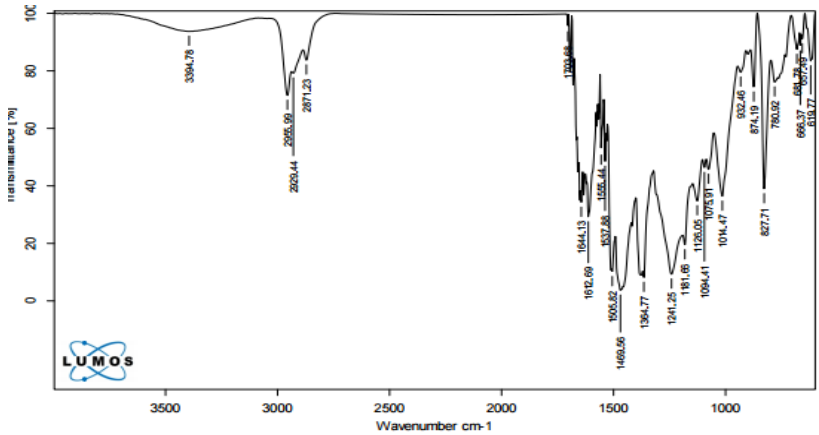


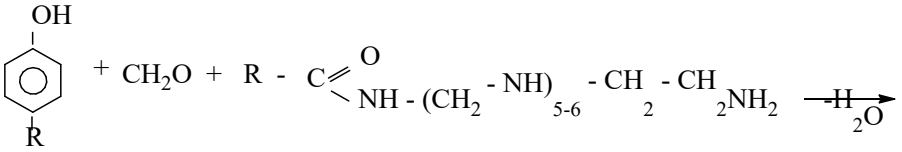
Figure 10. IR-spectrum of point 1 of APhFO modified by amidoamine based on DNPA and PEPA in a molar ratio of 1:1

Analysis of the IR-spectrum of point 1 showed that the spectrum contains absorption bands at 780, 827, 874, 1612 cm^{-1}, characteristic for C–H bond of the substituted benzene ring; absorption bands at 1364, 1469, 2871, 2929, 2955 cm^{-1}

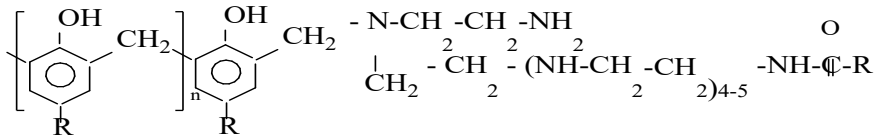
corresponding to C–H bonds of CH_3 and CH_2 groups; absorption bands at 1181 and 3394 cm^{-1}, respectively, referring to phenolic CO and OH groups, and there's also a band at 1644 cm^{-1} , characteristic for C=O bond of amide. Besides, the spectrum contains absorption bands at 1505, 1537, 1555 cm^{-1}, related to N–H bonds. The band at 1241 cm^{-1} corresponds to C–N bond. The IR spectrum of the sample contains absorption bands of very weak intensity at 932 and 1703 cm^{-1}, which respectively refer to acid OH and CO groups. IR spectra of all 5 points are almost identical.

The scheme for obtaining APhFO modified by amidoamines can be represented as follows:

Scheme 2



Amidoamine, obtained on the basis of DNPA and PEPA in a molar ratio of 1:1.



Similarly, the studies were carried out for other samples, the results confirmed the homogeneity of the synthesized oligomeric

The results of gel chromatographic molecular weight distribution of APhFOs modified by amidoamines based on DNPA and PA were studied. In the synthesis of all the above oligomers, the modifiers were taken in an amount of 0.1 mol per 1 mol of the alkylphenol component. All samples were oligomers of the novolac type, where during their synthesis the molar ratio of alkylphenols to formaldehyde was 1:0.85. The MWD results are set into the table 8.

Table 8.

MWD parameters of APhFO modified by amidoamines on the basis of DNPA and PA

№	Oligomer composition	Fractional composition, %	MWD		
			Mw	Mn	Mw/Mn
1	APhFO, modified by amidoamine based on DNPA:PEPA in a molar ratio of 1:1	3.85 96.15 -	8474 959 1255	7333 607 632	1.15 1.58 1.98
2	APhFO, modified by amidoamine based on DNPA:PEPA in a molar ratio of 3:1	4.54 95.46 -	6687 852 1120	6220 575 602	1.07 1.48 1.86
3	APhFO, modified by amidoamine based on DNPA:PEPA in a molar ratio of 5:1	2.73 97.27 -	5319 680 782	5040 467 485	1.05 1.45 1.61
4	APhFO, modified by amidoamine based on DNPA:TETA in a molar ratio of 1:1	3.63 96.37 -	5220 677 831	4996 501 520	1.05 1.35 1.6
5	APhFO, modified by amidoamine based on DNPA:TETA in a molar ratio of 3:1	3.33 96.67 -	5134 674 871	4554 480 535	1.13 1.4 1.6
6	APhFO, modified by amidoamine based on DNPA:DETA in a molar ratio of 3:1	2.5 97.5 -	5377 648 825	4731 540 559	1.14 1.2 1.47

Analyzing the data in the table, the followings can be noted:

- APhFOs modified by amidoamines of various compositions consist of two fractions - high molecular weight (in small amounts) and low molecular weight (in large amounts);
- a decrease in the molecular weight of polyamines used for obtaining amidoamines, as well as an increase in the molar amount of acid when using the same polyamine, the MWD values decrease, a similar pattern was observed with a decrease in the molecular weight of the amine at the same acid:amine molar ratio;
- some fractions have a narrower MWD value, and a broader final product;
- based on the analysis of the results, it can be assumed that the number of APhFO fragments repeated in high-molecular fractions is ~20-35, and in low-molecular fractions ~ 3-5.

The inhibiting properties of APhFO modified by amidoamines were studied in T-30 turbine oil in the amount of 5 and 10%. The

analyses were carried out in accordance with ГОСТ 9.054-75 ("Conservative oils, lubricants and inhibited film-forming petroleum compositions") using "St-10" metal plates in Г-4 hydrochamber, seawater and 0.001% aqueous solution of H_2SO_4 until the first corrosion foci appear. The research results are presented in the table 9.

Table 9.

Parameters of APhFO, modified by amidoamines as corrosion inhibitors in T-30 turbine oil

№	Composition of conservative fluid	Content in oil, %	Г-4, days	Seawater, days	0.001% aq.solution H_2SO_4, days
1	T-30	100	34	15	9
2	T-30 APhFO, modified by amidoamine (based on DNPA:DETA=3:1)	90 10	145	73	119
3	T-30 APhFO, modified by amidoamine (based on DNPA:TETA=1:1)	90 10	155	76	104
4	T-30 APhFO, modified by amidoamine (based on DNPA:TETA=2:1)	90 10	164	87	114
5	T-30 APhFO, modified by amidoamine (based on DNPA:TETA=3:1)	90 10	175	100	125
6	T-30 APhFO, modified by amidoamine (based on DNPA:TETA=4:1)	90 10	185	112	134
7	T-30 APhFO, modified by amidoamine (based on DNPA:PEPA=1:1)	90 10	185	83	104
8	T-30 APhFO, modified by amidoamine (based on DNPA:PEPA=2:1)	90 10	193	94	115
9	T-30 APhFO, modified by amidoamine (based on DNPA:PEPA=3:1)	90 10	205	105	125
10	T-30 APhFO, modified by amidoamine (based on DNPA:PEPA=4:1)	90 10	216	115	137
11	T-30 APhFO, modified by amidoamine (based on DNPA:PEPA=5:1)	90 10	229	127	148

Based on the data in the table, the following conclusions can be drawn:

- APhFOs modified by amidoamines of various compositions have a longer-lasting effect of corrosion protection in comparison to unmodified compounds;
- an increase in the molar amount of amidoamine per 1 mol of alkylphenols cause an increase in the anticorrosive effect of conservative fluids;
- APhFOs modified by amidoamines synthesized on the basis of DPNA and TETA possess a high anticorrosive effect;
- a satisfactory result of anti-corrosion protection belongs to the conservation fluid consisting of turbine oil T-30, APhFO, modified by amidoamine based on DNPA and PEPA (obtained in a molar ratio of 5:1) - the appearance of the first corrosion foci was observed in the hydrochamber after 229 days, in seawater after 127 days, in 0.001% aqueous solution of H2SO4 after 148 days.

3. Synthesis and study of the properties of monoalkyl (C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on fatty acids of vegetable oils and polyamines.

Sunflower, corn, cotton, palm and soybean oils were used to obtain fatty acids of vegetable origin. Obtainment of a mixture of acids from vegetable oils was carried out by saponification with 20% solution of sodium hydroxide at 95-97°C, followed by neutralization with hydrochloric acid. The processes of synthesis of imidazolines based on fatty acids obtained from various vegetable oils and APhFO modified by them corresponds to those specified in the previous section. The final products of synthesis are resinous substances of light and dark brown color that are highly soluble in polar, non-polar solvents and oils. Vegetable oils are basically identical in qualitative composition, therefore, studies are considered on the example of APhFO modified by imidazolines based on fatty acids isolated from sunflower oil and polyamines.

The structure of the synthesized products was investigated on IR Fourier spectrometer in the wavelength range of 600-4000 cm^{-1} in

comparison with the initial components. Spectral studies were fully proved the composition of imidazolines.

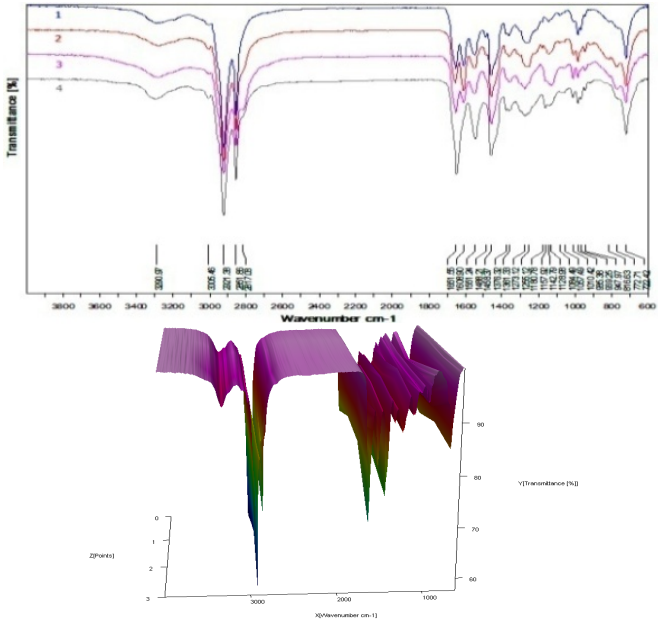


Figure 11. IR-spectra and 3d images of the spectra of imidazolines synthesized on the basis of acids obtained from sunflower oil with DETA-1, TETA-2, PEPA-3 and 4 in molar ratios 1: 1, 1: 1, 1: 1, 2:1, correspondingly.

The spectra (fig. 11) show the ranges of absorption bands of stretching vibrations of C=N bonds 1637-1654 cm^{-1}, stretching vibrations of C = C bonds 3002-3017 cm^{-1}, bending vibrations 722, 766-771, 1358-1361, 1376-1379, 1457-1465 cm^{-1} and stretching vibrations 2851-2852, 2871, 2921-2922 C-H bonds of CH_3- and CH_2- groups, deformation 1546-1553, 1610 cm^{-1} and stretching 3277-3279, 3288-3294 cm^{-1} vibrations of N-H bonds. Fixation of the data and disappearance of absorption bands corresponding to stretching vibrations of C=O groups at 1707 cm^{-1}, O-H bonds of carboxyl groups at 935-936 cm^{-1}, carboxyl groups at 2580, 2667, 2674 cm^{-1} observed in the spectra of fatty acids of vegetable oils, as well as the appearance of absorption bands at 1637-1654 cm^{-1}

corresponding to stretching vibrations of C = N bonds confirms the process of obtaining imidazolines.

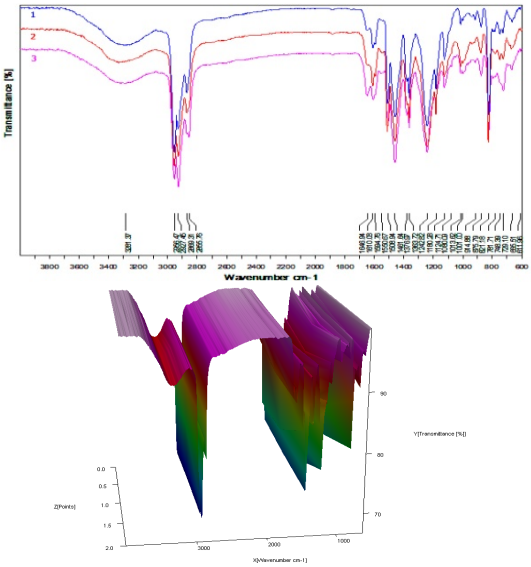


Figure 12. IR-spectra and 3d images of APhFO spectra modified by imidazolines based on fatty acids of sunflower oil with DETA in a molar ratio of 1:1 in the amount of 0.1 (1), 0.2 (2), 0.3 (3) per 1 mole of alkylphenols.

The spectrum (fig. 12) shows absorption bands corresponding to deformation 725-729, 1363-1364, 1376-1377, 1461-1462 cm^{-1} and stretching 2855, 2869-2870, 2924-2926, 2955-2956 cm^{-1} vibrations of C-H bonds of CH_2- and CH_3-groups, deformation 1504-1512 cm^{-1} and stretching 3281, 3288, 3333 cm^{-1} vibrations of N-H bonds, stretching vibrations 1645-1647 cm^{-1} C=N bonds of imidazoline ring, deformation vibrations of C-H bonds of the substituted benzene nucleus at 748-749, 821-828, 875-878, 1594, 1609-1611 cm^{-1}. Peaks at 1180, 1241-1242, 3281-3288, 3333 cm^{-1} express absorption bands inherent in stretching vibrations of phenol C-O and O-H bonds. The absorption bands at 3288, 3333 cm^{-1} in the spectrum also express N-H bonds of amine fragments.

Analysis of the spectra confirmed the presence of absorption bands related to both imidazoline and alkylphenolformaldehyde fragments in the structure of oligomeric macromolecules. The

dependence of the optical densities of the main functional fragments (C=N, alcohol and phenolic C-O groups) on the qualitative and quantitative composition, the composition of imidazolines and the number of moles per 1 mole of alkylphenols was studied, and the corresponding conclusions were drawn. Accordingly, modification process occurs on the scheme given in the previous section. Determination of the structure and structural features was carried out exclusively for all imidazolines and APhFOs modified by them, homogeneity of the oligomeric system was found using IR-spectroscopy.

The change in the content of some functional fragments was determined by calculating the optical densities of the corresponding absorption bands. The results are shown in the table 10.

Table 10.

Optical densities of absorption bands of the main bonds

№	Sample composition	$D_{1697-649}$ cm^{-1} (C=N)	D_{1000} cm^{-1} (C-O)	$D_{1012-1013}$ cm^{-1} (C-O)
1	APhFO, mod.by imidaz. based on FAPO and DETA=1:1 /0.1 mol modifier per 1 mol APh/	0,024	0,013	0,018
2	APhFO, mod.by imidaz. based on FAPO and DETA=1:1 /0.2 mol modifier per 1 mol APh	0, 039	0,037	0,040
3	APhFO, mod.by imidaz. based on FAPO and DETA=1:1 /0.3 mol modifier per 1 mol APh /	0,050	0,026	0,025
4	APhFO, mod.by imidaz. based on FAPO and TETA=1:1 /0.1 mol modifier per 1 mol APh /	0,061	0,030	0,034
5	APhFO, mod.by imidaz. based on FAPO and TETA=1:1 /0.2 mol modifier per 1 mol APh /	0,048	0,026	0,026

As is evident from the table, in all cases:

- optical densities corresponding to imidazoline fragments (C=N) increase (samples 1, 2, 3) by an increase in the molar amount of the modifier per 1 mol of alkylphenols;
- optical densities corresponding to C=N bonds were higher

(samples 1,4; samples 2,5) in the second case when using the same amount of imidazolines obtained on the basis of FAPO with DETA and TETA;

- no significant regularities were observed in the series of optical densities corresponding to the absorption bands of C-O bonds of alcohol groups (CH_2OH).

Molecular weight distribution in APhFOs modified by imidazolines based on fatty acids of sunflower oil with polyamines of various compositions was determined by gel permeation chromatography. The calculated chromatograms of the weight-average Mw and number-average Mn molecular weights are shown in table 11.

Table 11.

MWD indices of APhFO modified by imidazolines based on fatty acids of sunflower (FASO) and corn (FACO) oil with polyamines

№	Composition of the imidazolines used in the modification / number of moles per 1 mole of alkyl phenols /	Fractional composition, %	MWD			MM*(max)
			Mw	Mn	Mw/ Mn	Mn (at max peak)
1	2	3	4	5	6	7
1	FASO:DETA 1:1 /0.1/	17 11 72 -	5296 2407 730 1645	4702 2356 550 648	1.13 1.02 1.33 2.54	615 (13.25)
2	FASO:DETA 1:1 /0.2/	-	1437	665	2.16	530 (13.5)
3	FASO:DETA 1:1 /0.3/	14 86 -	7174 710 2073	6615 490 818	1.08 1.45 2.53	708 (13.0)
4	FASO:TETA 1:1 /0,1/	5 95 -	7611 1098 1572	7171 700 841	1.06 1.57 1.87	710 (13.0)
5	FASO:TETA 1:1 /0.2/	5 95 -	7012 918 1307	6517 600 657	1.07 1.53 1.99	(13.25)
6	FASO:PEPA 1:1 /0.1/	10 13 77 -	6749 4992 2573 1769	6325 4194 1956 860	1.07 1.19 1.31 2.05	460 (12.75)

Continuation

1	2	3	4	5	6	7
7	FASO:PEPA 2:1 /0.1/	5 95 -	8869 1076 1474	8366 628 619	1.06 1.71 2.38	615 (13.25)
8	FACO:DETA 1:1 /0,1/	35 65 -	6384 1068 3055	5375 744 1097	1.19 1.43 2.78	6130 (9.25) 460 (12.75)
9	FACO:DETA 1:1 /0,2/	5 95 -	9228 1344 1883	8935 692 788	1.03 1.94 2.39	708 (13.0)
10	FACO:DETA 1:1 /0,3/	4 96 -	8306 1394 1713	7887 875 911	1.05 1.59 1.88	460 (12.75)
11	FACO:TETA 1:1 /0,1/	8 92 -	9914 1452 2105	9396 862 932	1.05 1.68 2.16	460 (12.75)
12	FACO:TETA 1:1 /0,2/	4 96 -	7918 1330 1624	7654 788 821	1.03 1.69 1.98	945 (12.5)
13	FACO:PEPA 1:1 /0,1/	-	1942	975	1.99	945 (12.5)
14	FACO:PEPA 2:1 /0,1/	16 84 -	7736 1327 2440	6970 905 1065	1.1 1.47 2.29	460 (12.75)

The data on the table show the following regularities in the molecular weight distribution of the modified APhFO:

- APhFO modified by imidazolines of various compositions mainly consist of 2 fractions – high-molecular (a small amount, comparatively), and low-molecular weight fractions (a large amount).

- high molecular weight fraction of all samples is characterized by a narrower polydispersity in comparison with the low molecular weight fraction;

- the final polydispersity for oligomers modified by imidazolines obtained on the basis of fatty acids with DETA is higher in comparison with oligomers of a different composition;

- despite a large amount of high-molecular fractional

composition of the oligomers, a high value of the molecular weight indices in relation to 1 mole of alkylphenols with a stable amount of the modifier is observed in the samples of oligomers modified by imidazolines obtained on the basis of fatty acids with TETA and PEPA;

- based on the results of studies of final values of molecular weights, it can be assumed that the average number of alkylphenol-formaldehyde fragments in oligomers obtained by modification with imidazolines based on fatty acids of sunflower oil with polyamines ranges from 4-9. In the case of corn oil fatty acids, this number ranges from 5-14.

Thermogravimetric analysis was carried out for the purpose of studying thermal stability of APhFO modified by imidazolines based on fatty acids of sunflower oil with polyamines. Dependence of the thermal properties on the composition was determined in comparison with the corresponding indicators of unmodified APhFO. Digital indices of the TGA curves were set into tables 12 and 13.

Table 12.

Dependence of the residual mass of APhFO modified by imidazolines based on fatty acids of sunflower oil with polyamines on temperature

№	Composition of imidazolines used for modification (amount of imidaz. per 1 mol of alkylphenol)	Temperature, 0C					
		100	200	300	400	500	600
		Residual mass, %					
1	Unmodified APhFO	105	100	82	32.5	15	13.74
2	FASO:DETA=1:1 (0.1)	105	101.5	80	42	15	12.78
3	FASO:DETA=1:1 (0.2)	110	103.75	82	55	25	23
4	FASO:TETA=1:1 (0.1)	106.5	102	80	42	16	14.63
5	FASO:PEPA=1:1 (0.1)	124	116	95	65	44	44.7
6	FASO:PEPA=2:1 (0.1)	112	105	82.5	56	26.5	24.92

Table 13.

Heat effects and stages of thermal destruction of APhFO modified by imidazolines based on fatty acids of sunflower oil with polyamines in the temperature range of 25-650°C

Destruction stages	Composition of imidazolines used for modification (amount of imidazoline per 1 mol of alkylphenol)	Destruction on set temperature, ^{0}C	Destruction end temperature, ^{0}C	Destruction max.temperature, ^{0}C	Heat exhange area, мkVs/mg
I	Unmodified APhFO	337.9	403.7	369.6	-785.8 (32.5-450.2)oC
I II	FASO:DETA=1:1 (0.1)	238.7 340	310 488.7	273 392.2	-749.2 (63.3-521.3)oC
I II	FASO:DETA=1:1 (0.2)	179.1 348.3	266.5 483.8	233.8 384.6	-1633 (55.5-488.9)oC
I II	FASO:TETA=1:1 (0.1)	181.5 323.2	293.6 485	260.5 383.7	-1215 (61.5-509.8)oC
I II	FASO:PEPA=1:1 (0.1)	166.9 330.3	279.1 499.1	225.5 377.0	-3027 (109.3-442.2)oC
I II	FASO:PEPA=2:1 (0.1)	181.9 334.0	281.0 493.2	237.4 397.2	-1496 (76.4-489.2)oC

As is evident from the tables, thermal destruction of all the studied samples generally begins at 300°C, becomes significant at 400°C and deepening at 500°C, stabilizes at 600°C. Modified APhFO have a higher thermal stability compared to unmodified ones (for example, a sample with a residual mass at 600°C equals to 44.7%). Weight loss is accompanied by evidence of cleavage endo-effects, and it's mainly observed above 40°C. Even if no sharp differences are observed in the maximum values of destruction temperatures in individual stages, but absolute value of the area corresponding to the change in heat takes on a higher value with an increase in molecular weight of amine compound used in the preparation of imidazoline - a modifier, that is, more energy is spent for destruction.

Anticorrosive efficiency of conservative fluids based on turbine oil T-30 and APhFO, modified by imidazolines based on fatty acids of various vegetable oils (sunflower, corn, cottonseed, palm, soybean) and polyamines was studied. The best results are set in table 14.

Table 14.

Comparative characteristics of anticorrosive effectiveness of APhFOs modified by imidazolines based on fatty acids of vegetable oils

№	Composition of conservative fluids	Content in oil, %	Climate chamber Corrosion box 1000E" (condensation regime), days	Sea-water, days	0.001% aq. sol. H_2SO_4, days
1	2	3	4	5	6
1	T-30	100	34	15	9
2	T-30 APhFO mod. by imidaz. FASO:DETA = 1:1 /0.3 mol to 1 mol AP/	90 10	228	187	199
3	T-30 APhFO mod. by imidaz. FASO:TETA= 1:1 /0.1 mol to 1 mol AP/	90 10	485	324	372
4	T-30 APhFO mod. by imidaz. FASO:PEPA= 1:1 /0.1 mol to 1 mol AP/	90 10	259	221	234
5	T-30 APhFO mod.by imidaz. FASO:PEPA= 2:1 /0.1 mol to 1 mol AP/	90 10	267	230	243
6	T-30 APhFO mod.by imidaz. FACO:DETA = 1:1 /0.3 mol to 1 mol AP/	90 10	365	301	310
7	T-30 APhFO mod.by imidaz. FACO:TETA = 1:1 /0.1 mol to 1 mol AP/	90 10	324	253	269
8	T-30 APhFO mod.by imidaz. FACO:PEPA= 1:1 /0.1 mol to 1 mol AP/	90 10	186	157	166

Continuation

1	2	3	4	5	6
9	T-30 APhFO mod.by imidaz. FACO:PEPA = 2:1 /0.1 mol to 1 mol AP/	90 10	220	168	177
10	T-30 APhFO mod.by imidaz. FAPO:DETA=1:1 /0.2 mol to 1 mol AP/	90 10	139	99	104
11	T-30 APhFO mod.by imidaz. FAPO:TETA=1:1 /0.2 mol to 1 mol AP/	90 10	300	238	255
12	T-30 APhFO mod. by imidaz. FAPO:PEPA=1:1 /0.1 mol to 1 mol AP/	90 10	396	307	321
13	T-30 APhFO mod. by imidaz. FAPO:PEPA=2:1 /0.1 mol to 1 mol AP/	90 10	371	281	296
14	T-30 APhFO mod. by imidaz. FACtO:DETA = 1:1 /0.2 mol to 1 mol AP/	90 10	184	146	155
15	T-30 APhFO mod. by imidaz. FACtO:TETA = 1:1 /0.2 mol to 1 mol AP/	90 10	212	166	175
16	T-30 APhFO mod.by imidaz. FACtO:PEPA=1:1 /0.1 mol to 1 mol AP/	90 10	341	252	266
17	T-30 APhFO mod. imidaz. FACtO:PEPA= 2:1 /0.1 mol to 1 mol AP/	90 10	356	267	282
18	T-30 APhFO mod. by imidaz. FASbO:TETA= 1:1 /0.1 mol to 1 mol AP/	90 10	192	78	90

Note: FASO, FACO, FAPO, FACtO, FASbO are fatty acids of sunflower, corn, palm, cottonseed, soybean oils, respectively.

Sunflower oil is mainly composed of 87% unsaturated acids.

APhFO modified by imidazolines synthesized on the basis of fatty acids of sunflower oil and TETA showed the best results in the interaction of a mixture of acids with TETA. It doesn't exclude the formation of bisimidazolines that leads to increased protective effect. Modifiers using a mixture of the fatty acids of sunflower oil with PEPA in a ratio of 2:1, respectively, have the following anticorrosive protection activity.

The bulk of corn, cottonseed and soybean oils are also composed of triglycerides of unsaturated acids. Anticorrosive efficiency of APhFO modified by imidizolines based on fatty acids of these oils with polyamines in the composition of conservative fluids varies depending on the polyamine, the change in the molar ratio of acid:polyamine in the modifier, as well as on the number of moles of the modifier per mole of alkylphenols. For example, APhFO modified by imidazoline based on acid obtained from corn oil with DETA by the use in an amount of 0.3 mol per mole of alkylphenols, showed the best result, surpassing the compositions of conservative fluids containing APhFO modified by imidazolines based on the similar acid with TETA and PEPA, but in lower amounts in relation to alkylphenols. The composition of palm oil is dominated by triglycerides of saturated acids of 53.8%. This greatly affected the measures of effiicency for the protection of conservative fluids with their participation. Among conservative compositions containing APhFO modified by imidazolines based on acids obtained from palm oil and polyamines, a satisfactory result corresponds to the modifier - the composition of fatty acid : polyethylenepolyamine in a molar ratio of 1:1 (sample 22). Possibly, this is facilitated by the high content of the acid component, as well as the polyfunctionality of the amine containing of a modifier. Since the more C=C double bonds, polar amine fragments and imidazoline rings in the composition of oligomeric macromolecules, the higher the protective efficiency. The above structural elements lead to high adhesion and formation of a dense protective layer on the metal surface. An increase in the acid content in the composition of imidazoline (sample 23) leads to a slight deterioration of similar indicators, the explanation of which is given above.

Considering the table, it should be noted the dependence of the inhibitory properties of modified APhFOs on the difference in fatty acid composition (content of saturated and unsaturated acids) of individual vegetable oils in imidazolines, functionality of polyamines and the length of the polyamine chain, as well as on the number of moles of the nitrogen-containing modifier in relation to alkyl phenols and the content of oligomers in mineral oil.

4. Synthesis and study of APhFO modified by imidazoline based on individual carboxylic acids

It was interesting to study the inhibitory properties of APhFO modified by imidazolines based on individual carboxylic acids of tridlycerides of almost all of the studied oils, in the composition of conservative fluids. Modification processes of APhFO with imidazolines based on palmitic acid, which is a representative of saturated and oleic acid, a representative of unsaturated carboxylic acids, were carried out, their structures and physicochemical characteristics were studied. For AFhFOs modified with imidazolines based on individual carboxylic acids and polyamines, the change in the amount of the used modifier, as well as the difference in the compositions of the imidazolines, did not affect the physicochemical parameters. The relative density, the content of non-volatile substances, the Ubbellode dropping point are very close. When determining the solubility, non-polar (benzene, gasoline, white spirit, T-30 turbine oil), polar (ethanol, dimethylformamide) and mixed (dioxane) solvents were used. Absolute solubility with the formation of a transparent solution for all studied APhFO samples modified with imidazolines based on palmitic acid and polyamines was observed in dioxane, especially for samples where the amount of modifier used was 0.2 mol per one mol of alkyl phenols. Some samples are poorly soluble in ethanol, with T-30 turbine oil, all the samples under study form a turbid, stable mixture, and are readily soluble in other non-polar solvents. AFhFOs modified by imidazolines based on oleic acid and polyamines are characterized by unsatisfactory solubility in non-polar media. Consideration of the

results of the analysis of IR spectroscopy indicate the similarity of the scheme for the synthesis of modified APhFOs with those described in the previous sections.

Inhibitory properties of APhFOs modified by imidazolines of the above mentioned compositions were investigated in turbine oil T-30 in the amount of 5 and 10%. The analyzes were carried out on steel plates 08Ю in a climatic chamber "Corrosion Box" in the mode of air condensation until the appearance of the first corrosion foci. The research results are set into table 15.

Table 15.

Determination of the duration of anti-corrosion protection of conservative fluids based on turbine oil T-30 and APhFO modified by imidazolines based on oleic (Ol.A) and palmitic (Pm.A) acids with polyamines

№	Composition of conservative fluids	%	"Corrosion box 1000E" (condensation regime), days
1	Turbine oil T-30	100	34
2	T-30 + APHFO mod.by imidaz. PmA:DETA=1:1 /0.1 mol to 1 mol AP /	90 10	124
3	T-30 APHFO mod.imidaz. PmA:TETA=1:1 /0.2 mol to 1 mol AP/	90 10	137
4	T-30 APHFO mod.imidaz. PmA:PEPA=1:1 /0.1 mol to 1 mol AP/	90 10	115
5	T-30 APHFO mod.imidaz. OlA:DETA=1:1 /0.1 mol to 1 mol AP/	90 10	114
6	T-30 APHFO mod.imidaz. OlA:TETA= 1:1 /0.2 mol to 1 mol AP/	90 10	132
7	T-30 APHFO mod.imidaz. OlA:PEPA=2:1 /0.1 mol to 1 mol AP/	90 10	104

The conservative fluids containing APhFO, modified by imidazolines based on acids and TETA. The long-term protection

effect corresponds to conservative fluids with the use in an amount of 10%, which in the case of oleic acid (OlA: TETA = 1:1 with the use of 0.2 mol of imidazoline per 1 mol of alkylphenols) was 132 days, and in the case of palmitic acid with similar indicators - 137 days. Increase in the number of moles of the modifier per 1 mol of alkylphenols, and increase in the total percentage of the additive in the oil cause increase in the indicators of anti-corrosion protection.

5. Synthesis and study of anti-corrosion properties of monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines based on synthetic petroleum acids and polyamines

Modification of APhFO was carried out with imidazolines based on SPA and polyamines. The structure and inhibiting properties were studied in turbine oil T-30.

The structures of the oligomers were studied using IR-spectroscopy. Figure 13 presents IR-spectrum of APhFO, modified by imidazolines based on SPA and DETA.

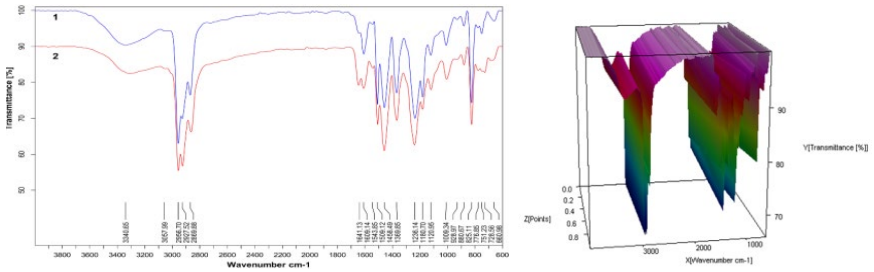


Figure 13. IR-spectra and 3 d-image of APhFO modified by imidazolines based on SPA with DETA in a molar ratio of 1:1 in the amount of 0.1 (1), 0.2 (2) per 1 mol of alkylphenols

As is evident from the figure, the spectra represent 728, 1368-1369, 1458-1459 cm^{-1} deformation vibrations, 2864-2869, 2925-2927, 2956 cm^{-1} stretching vibrations of CH bonds of CH_2- and CH_3-groups, deformation vibrations 1507-1509 cm^{-1} and stretching vibrations 3311, 3340 cm^{-1} of NH bonds, stretching vibrations 1641-1646 cm^{-1} of C=N bonds in the imidazoline ring, stretching

vibrations 1609-1610 cm^{-1} C-C bonds of the benzene ring, deformation vibrations 751, 724-725, 879-880 cm^{-1} C-H bonds of the benzene ring, stretching vibrations 1006, 1009 and 3311 and 3340 cm^{-1} of C-O and O-H alcohol groups. The peaks at 1180-1181, 1236-1239 and 3311, 3340 cm^{-1} reflect absorption bands corresponding to the stretching vibrations of C-O and O-H bonds of alkylphenol. The contours of the peaks at 3311, 3340 cm^{-1} of O-H bonds of alcohol and phenol make it possible to assume the superposition of absorption bands with the absorption bands of the N-H bonds of amine fragments.

The physic-chemical properties of APhFOs modified by imidazolines based on SPA and polyamines were studied. The results are set into table 16.

The analyses to determine the anticorrosive resistance of conservative fluids were carried out on steel plates 08Ю in a climatic chamber "Corrosion Box" in the mode of air condensation until the first corrosion foci appeared. Corrosion resistance lasts 118 days when APhFO modified by imidazoline based on SPA and DETA is added to turbine oil T-30, obtained at a molar ratio of 1:1 (0.1 mol of imidazoline per 1 mol of alkylphenols) in the amount of 10% and it's the best indicator in comparison with compositions of similar compositions modified by imidazolines on the basis of other PA. The results are relatively lower in relation to previous studies, therefore, analyzes were carried out with the addition of nitration products of $C_{14}H_{28}$ α-olefins in the amount of 2.5-5%, which led to a slight increase in indicators, but the patterns of protective efficacy did not change. Thus, the most effective compositions were conservative fluids containing APhFO modified by imidazoline based on SPA and DETA with nitration products of $C_{14}H_{28}$ α-olefins at a mass ratio of 1:1, where the anticorrosive resistance was 145 and 158 days, respectively.

Table 17 represents comparative indicators of conservative fluids of various compositions, including those containing amine components, as well as modified and unmodified APhFO.

Table 16.

Physico-chemical properties of APhFO, modified by imidazolines based on SPA and PA

№	Qualitative and quantitative composition of imidazoline (number of moles per 1 mol of alkylphenols)	Appearance	Relative density, d420, kg/m^3	Ubbelohde drop point, ˚C	Composition of non-volatile components, %	Solubility properties						
						Benzene	Gasoline	DMFA	Dioxana	White Spirit	Ethanol	Turbine oil T-30
1	SPA:DETA 1:1 (0.1)	Viscous mass of brown color	0.9616	31	95.203	+	+	+	+	+	+	+
2	SPA:DETA 1:1 (0.2)		0.9783	37	90.886	+	+	+	+	+	+	+
3	SPA: DETA 1:1 (0.1)	Viscous mass of light-brown color	0.9735	39	88.321	+	+	-	+	+	-	+
4	SPA:TETA 1:1 (0.2)		0.9754	40	88.133	+	+	-	+	+	-	+
5	SPA:PEPA 1:1 (0.1)	Viscous mass of brown color	0.9794	37	82.486	+	+	+	+	+	+	+
6	SPA:PEPA 2:1 (0.1)		0.9723	39	95.570	+	+	+	+	+	+	+

Note: + soluble, - insoluble.

Table 17.

Comparative characteristics of anticorrosive resistance of conservative fluids of different compositions

№	Composition of conservative fluid	Content in oil, %	Hydrochamber Г-4, days	Climate chamber Corrosion box 1000E" condensation regime, days	Sea water, days	0.001% aques. sol. H_2SO_4, days
1	2	3	4	5	6	7
1	T-30 Unmodified APhFO	90 10	160	-	21	29
2	T-30 Unmodified APhFO Amidoamine DNPA:PEPA=4:1	90 5 5	175	-	50	52
3	T-30 APhFO mod.by amidoamine DNPA:PEPA=5:1	90 10	229	-	127	148
4	T-30 APhFO mod. by imidaz. DNPA:PEPA=3:1	90 10	-	240	141	157
5	T-30 APhFO mod. by imidaz. DNPA:TETA=2:1	90 10	-	245	146	170
6	T-30 APhFO mod. by imidaz. DNPA:DETA=1:1	90 10	457	-	205	230
7	T-30 unmodified APhFO Amidoamine Nitrocompound of $C_{14}H_{28}$ olefins	90 3.3 3.3 3.3	220	-	113	125
8	T-30 APhFO mod. by imidaz. DNPA:PEPA=3:1 Nitroompound of $C_{14}H_{28}$ olefins	90 5 5	-	253	156	185

Continuation

1	2	3	4	5	6	7
9	T-30 APhFO mod. by imidaz. DNPA:TETA=2:1 Nitrocompound of $C_{14}H_{28}$ olefins	90 5 5	-	310	241	270
10	T-30 PhFO + APhFO mod. by imidaz. DNPA:TETA=2:1 Nitrocompound of $C_{14}H_{28}$ olefins	90 5 5	465		368	300
11	T-30 Imidazoline FASO:PEPA=1:1	90 10	162	-	96	84
12	T-30 APhFO mod. by imidaz. FASO:PEPA=1:1	90 10	-	259	221	234
13	T-30 APhFO mod. by imidaz. FASO:TETA =1:1	90 10	-	485	324	372
14	T-30 APhFO mod by imidaz. FACO:TETA=1:1	90 10	-	365	301	310
15	T-30 APhFO mod. by imidaz. FAPO:PEPA 1:1	90 10	-	396	307	321
16	T-30 APhFO mod. by imidaz. FACtO:PEPA=2:1	90 10	-	356	267	282
17	«Кормин» (Ст-10)		200	-	105	sust.
18	«РОСОЙЛ – 700М»		40	-	20	sust
19	«НГ-203Р»		100	-	44	sust.

As can be seen from table 13, regardless of the acidic component of modifiers (imidazolines, amidoamines), anticorrosive resistance indicators for the protection of conservative fluids based on modified PhFO and APhFO are superior to similar compositions containing amidoamines, imidazolines, unmodified APhFO, as well as compositions of the latter.

Figure 14 represents a process flow scheme for the complex production of conservative fluids using turbine oil T-30 and modified APhFO. The process flowsheet consists of several stages. The first stage is a scheme for the obtainment of fatty acids from the composition of vegetable oils. The second stage reflects the scheme for obtaining imidazolines on the basis of fatty acids of vegetable oils from the first stage or distilled natural petroleum acids with polyamines. The third stage is the process of polycondensation and modification of APhFO with imidazolines. The fourth stage reflects the process of compounding the pconservative fluid.

To carry out the first stage of the technological process, a certain amount of vegetable oil was loaded into the reactor 9 from the container 1. Further, a certain amount of sodium hydroxide solution was fed from tank 2. The temperature in the reactor was maintained at about 100°C. After the saponification process in the reactor, the products obtained, passing through the heat exchanger 11, were pumped by the pump 12 into the separating vessel with mechanical stirring 13, where the calculated amount of hydrochloric acid was supplied from the vessel 3. In the vessel 13, with stirring, the process of neutralizing the saponification products takes place. After stopping mechanical stirring, hot water was supplied to the container to wash the excess of hydrochloric acid from the container 4. Separation of the aqueous and organic phases was observed, water and hydrochloric acid were discharged from the bottom of the tank, pure acids on the side, which were pumped into the tank 17 by means of the pump 16. The required amount of acids was loaded into the reactor 23 from the tank 17 or 18. Polyamines were fed from tank 19 when the temperature in the reactor reached to 100°C. Further, the temperature in the reactor maintained at 220-240°C. The resulting products of synthesis were cooled to a certain temperature passing

through a heat exchanger 25 and pumped into a container with constant stirring and heating 27 by means of 26. In a reactor with a steam jacket 36, the process of polycondensation of APhFO with formaldehyde occurred with simultaneous modification by imidazolines. A certain amount of monoalkyl(C_8-C_{12})phenols and the required amount of formalin from vessel 28 were loaded into the reactor 31 from the vessel 30 by constant heating and stirring. Then, the calculated amount of hydrochloric acid was fed into the reactor from the vessel 29. Polycondensation process occurred in the reactor during an hour at about 100°C, the temperature in the reactor was lowered to 50°C using the refrigerator 31, and a certain amount of imidazolines was added into the system from the vessel 27. The modification products, passing through the heat exchanger 38 by means of the pump 39, were pumped into the vacuum collector 40, where were separated from the over-resin water, dried and pumped into the tank 47 under constant stirring by means of the pump 46. The required amount of T-30 turbine oil was pumped from reservoir 43 into reservoir 47 by pump 45 constantly stirring. If necessary, the calculated amount of nitrocompounds of α-olefins $C_{14}H_{28}$ from the tank 48 was also fed to the tank 47 with constant stirring using the measuring device 50. The finished conservative fluid was sent to the storage tank.

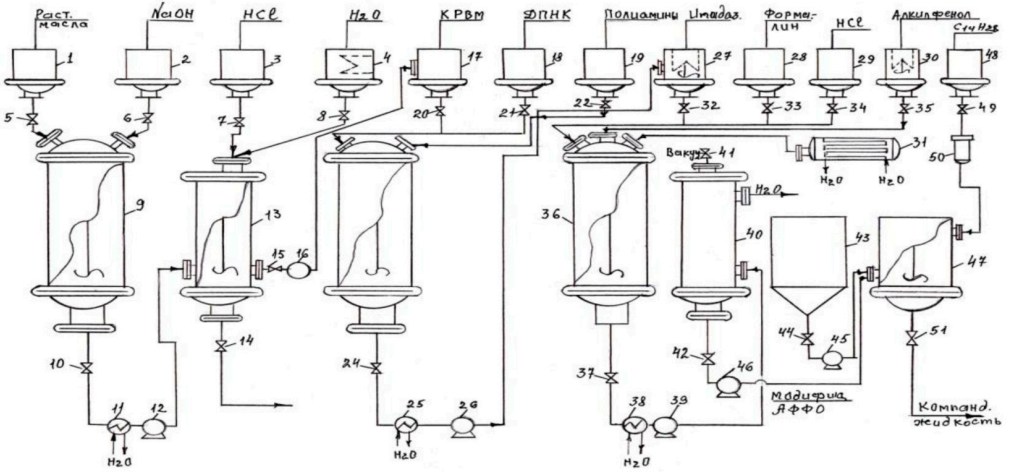


Figure 14. The process flow scheme for complex obtainment of conservative fluids based on turbine oil T-30 and monoalkylC_8-C_{12}phenolformaldehyde oligomers modified by imidazolines of different compositions

9, 23 – reactors, 36 – steam-jacketed reactor, 27, 30 – continuously stirred and heated tanks, 47 – continuously stirred tanks, 13 – separation capacity, 40 – vacuum collector, 43 – storage capacity, 31 - refrigerator, 50 – measuring tank, 1, 2, 3, 4, 17, 18, 19, 28, 48 – capacities, 11, 25, 38 – heat exchangers, 12, 16, 26, 39, 45, 46 – pumps, 5, 6 ,7, 8 ,10, 14, 15, 20, 21, 22, 24, 32, 33, 34, 35 ,37, 41, 42, 44 ,49, 51- valves

CONCLUSIONS

1. For the first time, phenol- and monoalkylphenolformaldehyde oligomers (with C_8-C_{12} alkyl substituents in para-position) of novolac type modified by imidazolines and amidoamines of various qualitative and quantitative compositions were synthesized; the process was optimized. Amine modifiers (containing imidazoline fragments) were used based on DNP, SPA, fatty acids of vegetable oils (sunflower, cottonseed, corn, soybean, palm), oleic and palmitic acids with PA - DETA, TETA, PEPA [2, 5, 6, 7, 13, 22, 25, 31, 32, 33, 35, 37, 38].
2. The structures, dependence of structural features (for example, the change in optical densities of the main functional fragments, such as C=N, C-O, N-H bonds) on the qualitative and quantitative composition of oligomers were investigated, a mechanism was proposed, including interaction of methylol groups of oligomer with amine groups of imidazoline [4, 12, 14, 27, 28].
3. Dependence of physico-chemical properties was studied including solubility in polar (ethanol, dimethylformamide, acetone, etc.), non-polar (benzene, toluene, white spirit, gasoline, turbine oil T-3) on the qualitative and quantitative composition of oligomers. Good solubility was found in non-polar solvents, including a sample of mineral oil, oligomers on a para-alkyl (C_8-C_{12})phenolic base in comparison with phenolic [8, 9, 11, 23].
4. The molecular weight distribution of modified phenol-, monoalkyl (C_8-C_{12})phenolformaldehyde oligomers was studied by gel permeation chromatography. Mainly two fractions were identified: high-molecular and low-molecular, where a high content of the latter is usually observed. In the case of PhFOs modified by imidazolines based on DNPA with polyamines, the number of repeating phenolformaldehyde fragments in the high-molecular fraction corresponds to ~30-35 and more, and in the low-molecular fraction ~ 5-7. In monoalkyl(C_8-C_{12})phenolformaldehyde oligomers modified by amidoamines, these parameters correspond to ~20-35 and ~3-5, and for imidazolines modified on the basis of vegetable oils fatty acids, the average number varies within ~ 4-14 [1, 3, 19 , 20].

5. Thermal stability of phenol-, monoalkyl (C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines and amidoamines up to 700°C in comparison with unmodified analogs was studied by TGA and DTA methods in an inert atmosphere, the dependence on the composition was also studied. The onset of thermal destruction for all samples was recorded at >300°C, deepens at 400-600°C, and stabilizes above 650°C. As a rule, modified oligomers are superior in thermal stability to unmodified oligomers. The multi-stage destruction was justified by the complex structure of oligomers. Conclusions were drawn on the release of volatile compounds at the first stage, decomposition of alkylphenol-formaldehyde chain in the second and, presumably, polyamine chain at the third stage of destruction [10, 17, 21, 23, 30, 36].

6. Corrosion resistance (ГОСТ 9.054-75) of conservative fluids based on turbine oil T-30 and phenol- and monoalkyl (C_8-C_{12})phenolformaldehyde oligomers modified by imidazolines and amidoamines of various compositions with the content of the latter 5 and 10% was studied in wet, saline and acidic media. A significant superiority was found both over the base and over analogs containing unmodified oligomers. For example,

- at a content of 10% phenolformaldehyde oligomer modified by imidazoline based on DNPA and DETA (molar ratio 1:1), in mineral oil T-30 the surface of steel St-3 was protected from corrosion in the hydrochamber Г-4 for 457 days , in seawater 205 days, in 0.001% aqueous solution of sulfuric acid for 230 days, which was several dozen times higher than those of the base [18, 29, 38].

7. High efficiency of the synthesized nitrogen-containing oligomers as corrosion inhibitors for steel St-10 and 08Ю was proven in T-30 oil in the condensation mode of the “Corrosion Box 1000E” climatic chamber, in seawater, in a 0.001% sulfuric acid solution. For example,

- at a content of 10% monoalkyl(C_8-C_{12})phenolformaldehyde oligomer modified by imidazoline based on acids obtained from sunflower oil with TETA (molar ratio 1: 1), the steel surface is protected from corrosion for 485 days, in sea water for 324 days and

at 0.001 % aqueous solution of sulfuric acid 372 days [26, 34].

8. Positive effect was noted for the presence of C_{14}-C_{28} α-olefin nitrocompounds in the composition. For example,

- with a content of 5% phenol- and monoalkyl(C_8-C_{12})phenol formaldehyde oligomer modified by imidazoline based on DNPA with TETA (molar ratio 2:1) and 5% of the products of nitration of C_{14}-C_{28} olefins, similar indicators are 465, 368 and 300 days, respectively [18, 29, 38];
- at 10% monoalkyl(C_8-C_{12})PhFO, modified by imidazoline based on SPA with DETA (molar ratio 1:1) corrosion resistance in the condensation mode of “Corrosion Box 1000E” climatic chamber lasts 118 days, and in the composition with nitrocompound 158 days.

9. The process flow scheme was proposed combining several stages, including separation of fatty acids from vegetable oils, preparation of imidazolines on their basis, as well as on the basis of DNPA, synthesis of phenolic oligomers modified by imidazolines, and preparation of conservative fluid.

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