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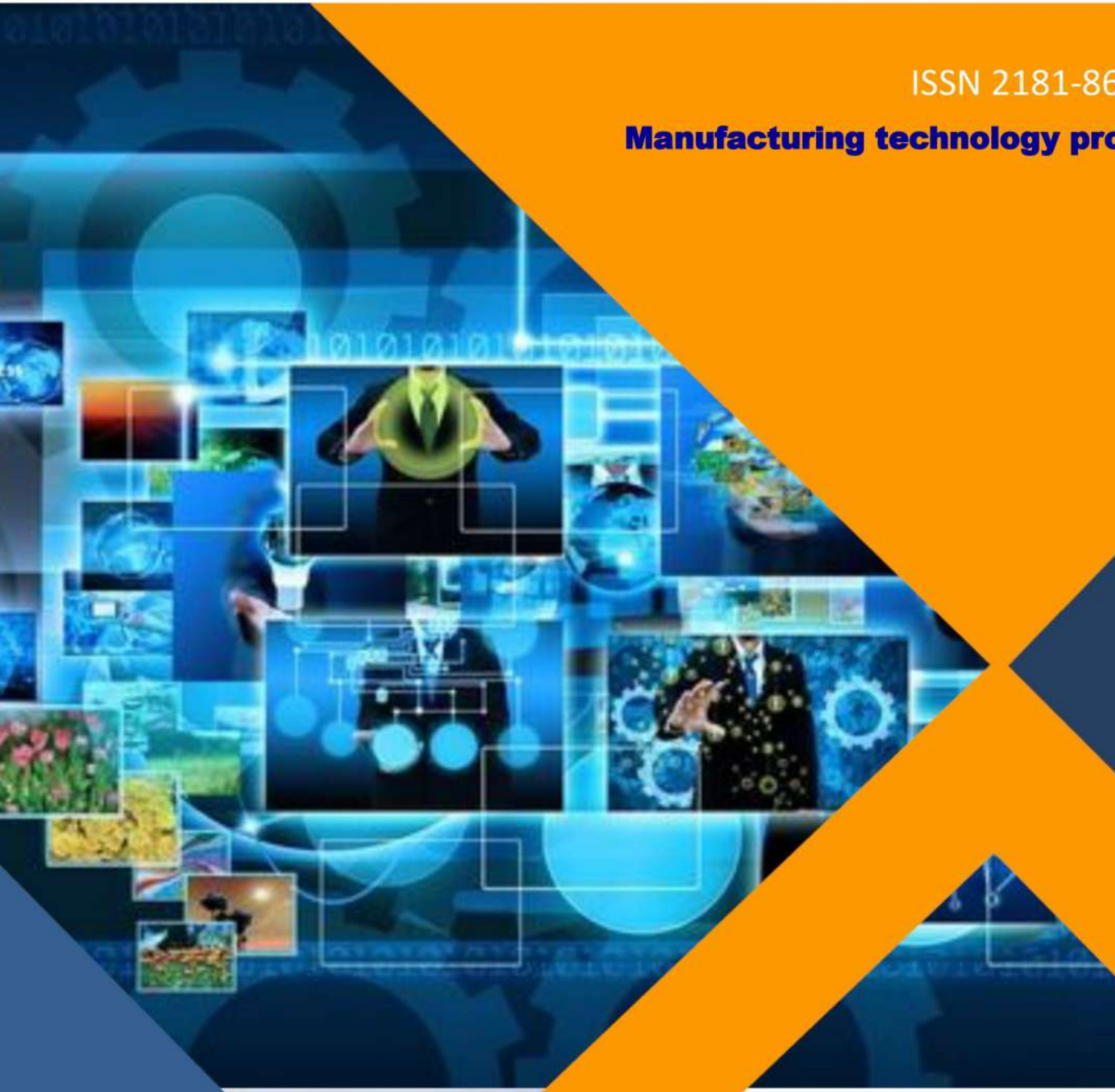
Manufacturing technology problems



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SYNTHESIS OF MELAMINE-FORMALDEHYDE RESINS MODIFIED WITH N-BUTANOL

YUSUPOV KUDRAT

The Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan
Phone.: (0890) 165-7377, E-mail.: qyusupov7177@gmail.com
Corresponding author

ERKABAEV FURKAT

Professor of Research Institute of Environmental and Nature Protection Technologies, Tashkent, Uzbekistan
E-mail.: erkabaevf@rambler.ru

ERGASHEV DILMUROD

Professor of International Institute of Food Technology and Engineering, Tashkent, Uzbekistan
E-mail.: dilmurod-ergashev2203@mail.ru

RAKHIMOV UMIDJON

Namangan Institute of Engineering and Technology, Namangan, Uzbekistan
E-mail.: rumid123456@gmail.com

NUMONOV MUHAMMADRAJAB

The International Institute of Food Technology and Engineering, Tashkent, Uzbekistan
E-mail.: qalampir2017@gmail.com

Abstract: The article discusses synthetic resins, specifically phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde resins, as well as the process of modifying them with n-butanol. Melamine-formaldehyde resins are particularly in demand in the paint and coatings industry, as they improve viscosity and gloss, thereby enhancing product quality.During the modification process, the addition of n-butanol can alter the physicochemical properties of the resins, improving their workability and the quality of the final products. Research results showed that the modified resins exhibit greater stability, higher gloss, and excellent viscosity. This expands their application possibilities in the paint and coatings industry.The findings indicate that modification with n-butanol enhances the properties of the resins, allowing them to meet modern requirements and standards. Therefore, this research is significant for the production of synthetic resins and the improvement of their quality.

Keywords: melamine, formaldehyde, phenol, urea artificial resin, melamine-formaldehyde, adhesion, evaporation, n-butanol.

Introduction. Currently, significant attention is being paid globally to the development of technologies for obtaining paint materials, synthesizing components used in their production, and improving their properties. Various paints, particularly automotive coatings, are in high demand in industrial enterprises, and their production process is quite complex. A significant portion of the components that enhance adhesion properties and gloss in high-quality paints is imported at the expense of foreign currency. The synthesis of these components and the production of essential products for the national economy based on positive research results will promote localization and reduce foreign currency expenditures on imports.

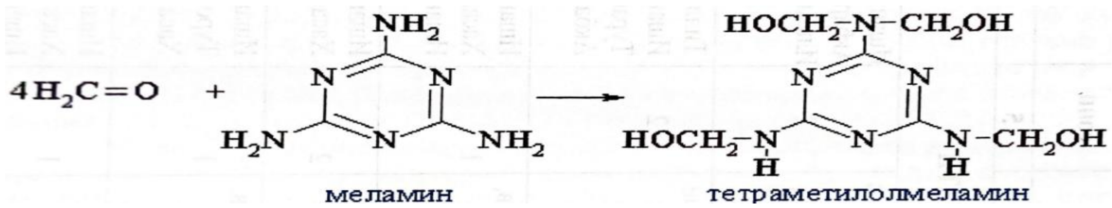
In Uzbekistan, research is being conducted on obtaining semi-finished products or components with high-quality properties for various paints using local or partially local raw materials. Theoretical and practical results have been achieved in developing technologies for their application. Particular emphasis should be placed on extracting various organic compounds, raw material components used in the production of organic products, and elements and compounds required for the national economy.

Among synthetic resins, melamine-formaldehyde resins, obtained under specific conditions from melamine and formaldehyde, are widely used in the industry. The production of melamine-formaldehyde resins occurs in several stages, with structural changes occurring at each step. The solution contains a mixture of melamine polymers that form hydrophilic melamine resin with a low degree of polycondensation. At the third stage of condensation, a hydrophobic fraction appears in the resin, which precipitates upon dilution with water. The proportion of the hydrophobic fraction gradually increases, requiring less and less water for precipitation. Over time, an optimal amount of water forms for hydrophobic resins deposited in the cold, leading to the resin's separation into two layers: the lower layer contains more resin and partially water, while the upper layer consists mainly of water and dissolved condensed methylol compounds. If the heating process continues, the delamination temperature of the formed resin increases, and the resin becomes cloudy, delaminating at its boiling point, indicating an intermediate degree of polycondensation.

Methods. The condensation rate of industrial melamine resins depends on several factors, including the pH level of the medium, the molar ratio of reagents during synthesis, the presence of compounds that slow down condensation (such as methanol), the presence of melamine hydrolysis or deamination products in the reaction mixture, various salts, and other components. One of the key factors influencing the rate and direction of condensation is the concentration of hydrogen ions. The condensation rate is lowest at pH 9–10 and increases with both rising and decreasing pH. In the pH range of 8.1–8.6, at a formaldehyde-to-melamine molar ratio of 3:1, a 0.1 unit decrease in pH results in a 10% acceleration of the reaction (at 830 min). At lower pH values, further changes have little impact on the reaction rate. At pH 4–6, condensation occurs very rapidly, forming a gel and precipitating amorphous polymers similar to methylene carbamide.

When melamine reacts with formaldehyde in a strongly acidic medium, methyleneamine salts initially form, which gradually transform into a hydrophilic colloidal solution with a molecular weight of 1700–4000. The formation of a colloidal solution occurs due to the appearance of additional charged condensate particles that resist aggregation. The stability of the resulting melamine solutions primarily depends on their concentration, and they remain stable even after drying.

The efficiency of the reaction in obtaining melamine-formaldehyde resin from melamine and formalin is closely related to the molar ratio of the components, the pH of the medium, and the temperature. The process reaches its maximum efficiency at a temperature of +82°C and a pH of 9–10:



Melamine reacts with formalin through polycondensation, where methylol derivatives of melamine are formed in the first stage of the reaction. Depending on the process conditions, 1 to 8 moles of formaldehyde can attach to 1 mole of melamine. The initial three moles of formaldehyde typically bind easily at relatively low temperatures, whereas the formation of hexamethylol melamine requires a larger amount of formaldehyde and a temperature of 80°C.

In the synthesis of melamine-formaldehyde resin, the optimal molar ratio of reactants is 1:8, with phthalic anhydride used as a catalyst. During the modification process, the highest product yield was achieved when 8 moles of formalin and 6 moles of n-butanol were used.

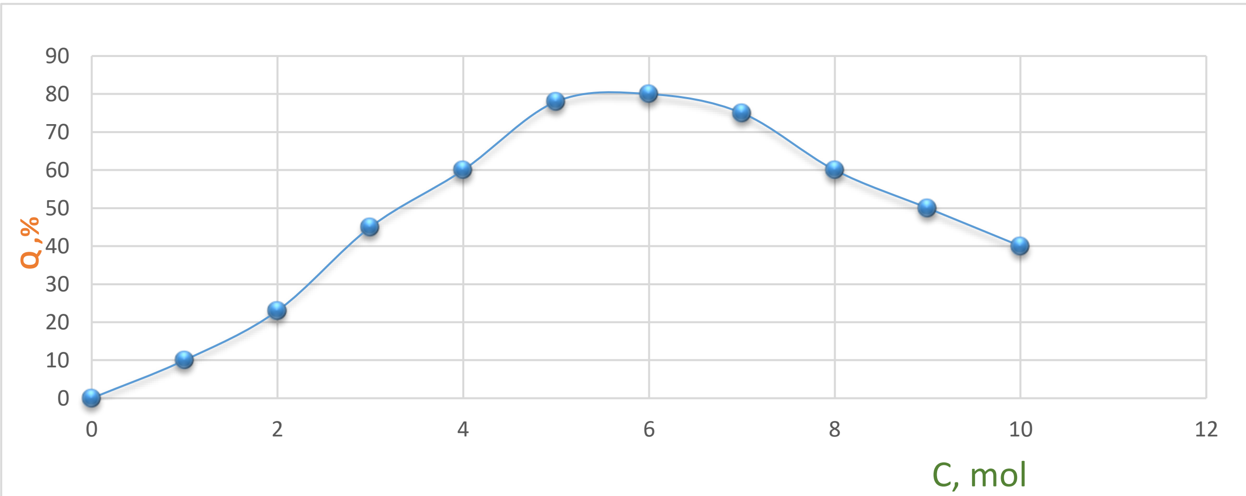


Figure 1. The Efficiency of Formalin Consumption at Different Ratios to 1 Mole of Melamine in the Synthesis of Melamine-Formaldehyde Resin

To improve the properties of melamine-formaldehyde resins, we conducted a study on their modification with n-butanol. In the production of coatings, melamine resins are first synthesized as methylolmelamine, which is then modified with n-butanol. However, in some cases, resins are prepared by simultaneously introducing all ingredients into a slightly acidic medium.

The properties of the obtained resin depend on the molar ratio of formaldehyde to melamine, the degree of esterification, the amount of acid catalyst, as well as the duration and temperature of the process. Typically, the synthesis of this resin involves adding 5-6 moles of formaldehyde per 1 mole of melamine, along with a slightly acidic amount of butanol. The reaction mixture is heated under reflux until the desired viscosity is achieved and the product becomes miscible with various hydrocarbons. Water is continuously removed through decantation, and the acid in the reaction medium is neutralized to the resin concentration level. The final resin should contain no more than 0.5% free water and formaldehyde. During the synthesis, 1 to 2 moles of butanol react with 1 mole of melamine, depending on the pH and temperature conditions.

The resulting polymer contains both ether and methylene linkages. The arrangement of structural units and bonds is speculative, as the actual polymer structure is more complex. Additionally, resins exhibit a three-dimensional structure rather than a planar one. Further polymerization is facilitated by the presence of numerous methylol groups capable of additional cross-linking. The condensation of two methylol groups with the release of one mole of water forms ether bonds, while the condensation of methylol groups bonded to nitrogen atoms results in methylene linkages.

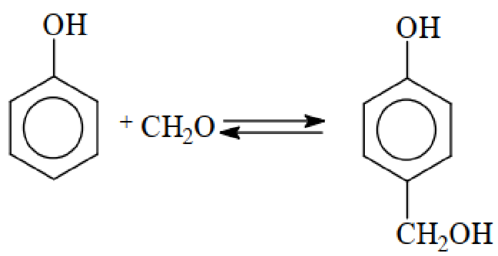
Next, the mixture is poured from a three-necked flask into a beaker and left undisturbed for 5-10 minutes to allow phase separation. The upper layer (aqueous phase) is removed using a pipette. After removal of the upper layer, the lower resin phase is dissolved in n-butanol at a predetermined ratio of 1:0.25 (resin:n-butanol), established under laboratory conditions.

An analysis of the obtained product was performed, and the comparative study of the physicochemical properties of the modified resin is presented in the table below.

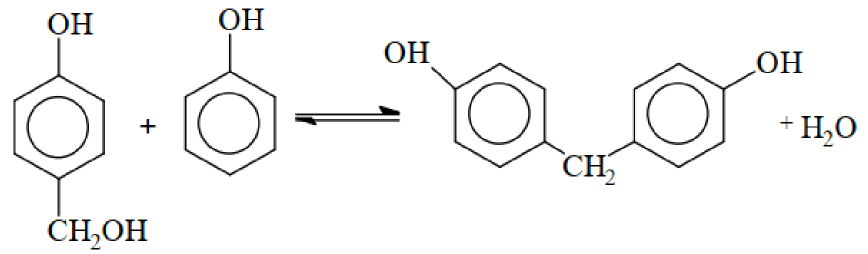
Resins are complex organic substances in terms of chemical composition. Natural resins are compounds secreted by plants as a result of normal physiological metabolism, with tropical plants, junipers, and pines being rich sources of natural resins. These resins are used in soap making, paper sizing, medicine, and the perfume industry. Today, synthetic polymers such as urea-formaldehyde and phenol-formaldehyde resins have largely replaced natural resins. Synthetic resins are widely used in the production of various plastic products.

The polycondensation of phenol with aldehyde involves a series of complex sequential and parallel reactions. The most typical and frequently occurring reactions include the hydroxymethylation of phenol by formaldehyde and the subsequent polycondensation of the resulting methylolphenols with each other and with oligomeric products. During hydroxymethylation, formaldehyde reacts at the ortho and para positions of phenol, where carbon atoms exhibit high electron density. Polycondensation reactions involving phenol occur at these active centers.

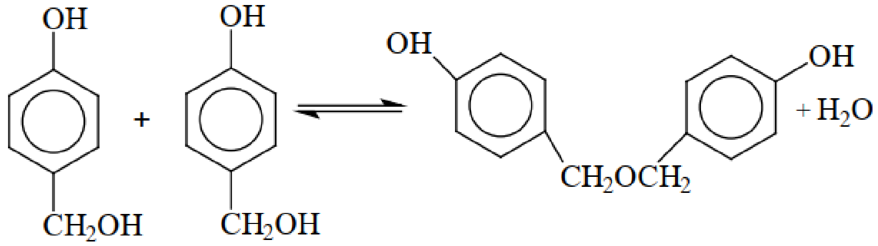
In the synthesis of phenol-formaldehyde oligomers, the main reactions occurring at the para position include the formation of methylol derivatives in the first stage:



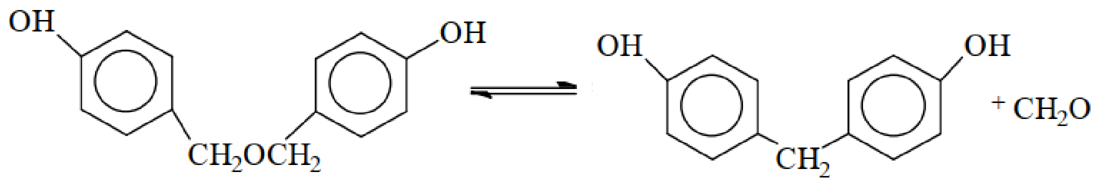
Subsequently, monomethylolphenols may undergo condensation reactions with phenol to form methylene bridges between phenolic nuclei:



Or may enter into a condensation reaction with each other:



Additionally, the cleavage of the dimethylene ether linkage (–CH_2–O–CH_2–) can lead to the release of formaldehyde, further contributing to the formation of methylene bridges.:



Similar transformations occur in the ortho positions of phenol during these reactions. In the absence of catalysts, the polycondensation of phenols with formaldehyde proceeds at a relatively low rate. Therefore, this reaction is often conducted in the presence of acidic or basic catalysts and, in some cases, with catalysts comprising metal salts.

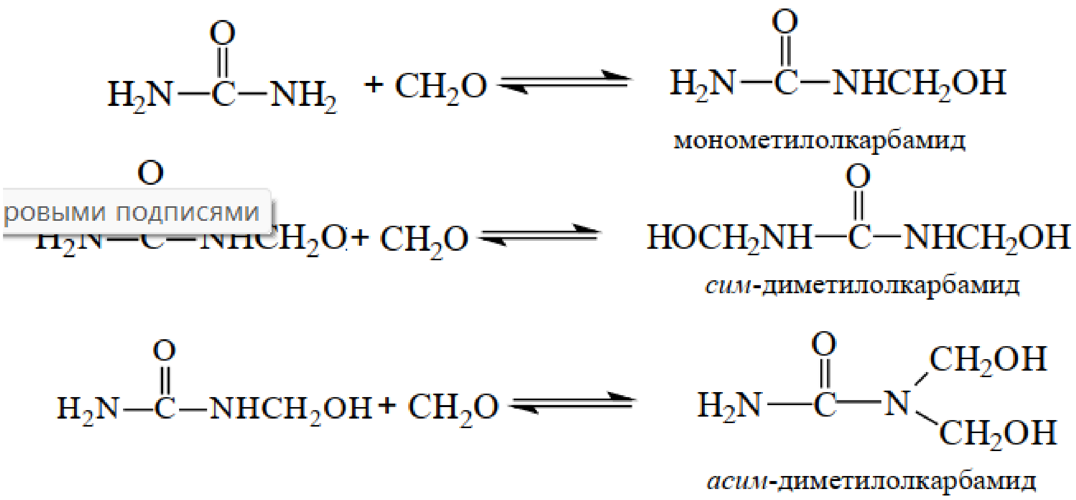
Depending on the polycondensation conditions, either resole (thermosetting) or novolac (thermoplastic) phenol-formaldehyde oligomers are formed. The primary factors influencing the formation of these types of oligomers include the nature of the catalyst and the molar ratios of reacting phenol and formaldehyde.

There are two main types of urea and melamine-formaldehyde oligomers: unmodified and modified with various alcohols. Modified oligomers are widely used in the paint and varnish industry.

Fundamental Principles of Urea-Formaldehyde Oligomer Synthesis

The polycondensation of urea with formaldehyde occurs in multiple stages. Initially, formaldehyde reacts with urea, leading to the formation of methylol derivatives through hydroxymethylation. Subsequently, the methylol derivatives of urea undergo condensation.

rea possesses two active centers ($H_2N–CO–NH_2$) and can theoretically bind up to four molecules of formaldehyde. When the reaction is conducted in a neutral or slightly alkaline medium (pH = 7), the initial products of urea's reaction with formaldehyde are methylol derivatives:



Polyamide Film Formers and the Importance of pH Control: It is crucial to carefully monitor the pH value, as side reactions involving formaldehyde can lead to a rapid decrease in pH.

Polyamides are heterochain polymers that contain repeating amide groups in their main polymer chain. These polymers can be synthesized through polycondensation reactions or ionic polymerization. Additionally, polyamides can be produced via the polyamidation reaction of polyamines with polycarboxylic acids and their derivatives, leading to polycondensation.

The polyamidation of carboxylic acids and their esters occurs as an equilibrium reaction, where low-molecular-weight byproducts, such as water or alcohol, are released. This reaction can be represented by the following general equation:

$$nHO–CO–R–CO–OH + nH_2N–R'–NH_2 \leftrightarrow HO[–CO–R–CO–NH–R'–NH–]_nH + (2n – 1)H_2O$$

Under specific conditions, this reaction proceeds in such a way that it constitutes the homopolycondensation of aminocarboxylic acids:

$$nH_2N–R–CO–OH \leftrightarrow$$
$$\leftrightarrow H_2N[–R–CO–NH–]_{n-1}R–CO–OH + (n – 1)H_2O$$

When carboxylic acid esters interact with amines, the polyamidization reaction can be expressed as follows:

$$nRO–CO–R–CO–OR + nH_2N–R–NH_2 \leftrightarrow$$
$$\leftrightarrow RO[–CO–R–CO–NH–R–NH–]nH + (2n – 1)ROH$$

The polyamidation of chlorangydrides is an almost unbalanced process that in practice varies over time:

$$nCl–CO–R–CO–Cl + nH_2N–R–NH_2 \rightarrow$$

$$\rightarrow Cl[-CO-R-CO-NH-R-NH-]_nH + (2n-1)HCl$$

When synthesizing polyamides from esters of carboxylic acids, it is usually carried out in their liquefaction (heated and diluted). In the synthesis of polyamides from carboxylic acids, polyamidation itself also occurs in liquefaction, but in the first exothermic stage of the process, the extraction of Amine salt is often carried out in a solvent with a low boiling level.

Table 1. Physical properties of modified melamine-formaldehyde resin

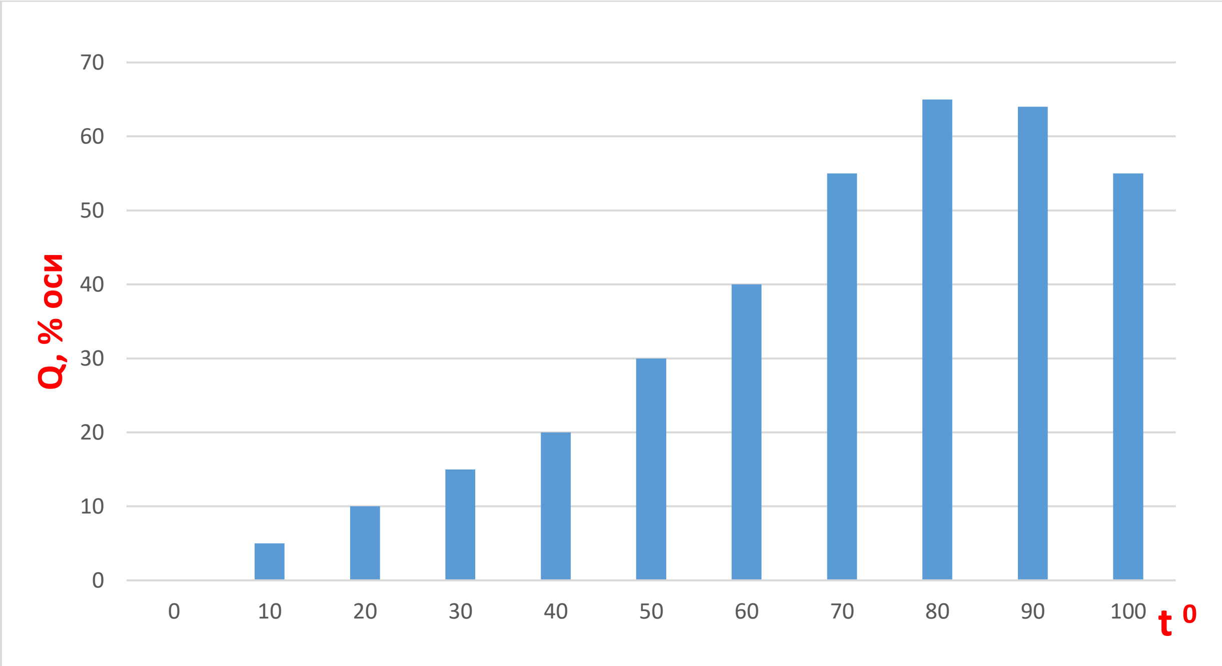
Physical properties	Parameters	Methods
Appearance	Transparent liquid	ASTM E284
Non volatile part	80-84%	DIN 55671 (Foil, 45 min/45°C)
None volatile part	78-82%	DIN EN ISO 3251 (Pan, 3 hrs/105°C)
Viscosity, 23°C	2300-7000 mPa·c	DIN EN ISO 3219
Free formaldehyde	< 0.6%	Titration with sulfite
Colour, APHA	≤ 70	DIN EN ISO 6271

Table 2. Chemical properties of modified melamine-formaldehyde resin

Erituvchilar	Eruvchanligi
Alcohol	fully soluble
Esters	fully soluble
Ketones	fully soluble
Aromatic hydrocarbons	fully soluble
Aliphatic hydrocarbons	Partly
Water	Not dissolve
Mixing	
Acrylic resin	Good
Alkidli smolalar	Very good
Poliefir smolalar	Very good
Epoksid smolalar	good

Results. The results of the visual inspection of the modified melamine-formaldehyde resin obtained during the research indicate that the product appears as a transparent liquid. It is fully soluble in alcohols, esters, ketones, and aromatic hydrocarbons, partially soluble in aliphatic hydrocarbons, and insoluble in water. It demonstrates good solubility in acrylic and epoxy resins and excellent solubility in alkyd and polyester resins. The water-insoluble fraction accounts for 78-84%, meeting the established requirements for modified melamine-formaldehyde resins.

Experimental studies on the effect of temperature on the product yield during the synthesis of melamine-formaldehyde resin modified with n-butanol revealed that the process proceeds efficiently within the temperature range of 75–85°C, resulting in a product yield of 60–66%.



Conclusion. The process of synthesizing melamine-formaldehyde, phenol-formaldehyde, and urea-formaldehyde resins, as well as the physicochemical processes of their modification with n-butanol, has been studied. Additionally, a comparative analysis of the produced modified melamine-formaldehyde resin with a commercial product conforming to GOST-9980.2 was conducted, yielding positive results.

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