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### SYNTHESIS OF ALKYD OLIGOMERS BASED ON BICYCLO[2,2,2] OCT-5-ENE-2,3-DICARBOXYLIC ACID ANHYDRIDE AND ITS APPLICATION FOR OBTAINING LACQUER COATINGS

The results of studies on the synthesis of modified by oil alkyd resin with the use of bicyclo [2,2,2] oct-5-ene-2,3-dicarboxylic acid anhydride as acylation agent in the polycondensation reaction with polyols for obtaining lacquer coatings and the study of their operational properties are presented in this article. It is found that the chemical modification of alkyd resin by replacing phthalic anhydride on bicyclic dicarboxylic acid anhydride allows to increase hardness, strength, adhesion of coatings formed on steel substrates.

**Introduction.** To improve the physical and mechanical properties of coatings based on alkyd oligomers the method of their chemical modification realised in different ways is widely used [1]. One of them is the variation of the chemical structure of the acyl part of the ester oligomer molecules [2]. This is achieved by the partial or complete replacement of phthalic anhydride used for the synthesis on other counterparts.

The partial or complete replacement of phthalic anhydride in the synthesis of polyesters modified by oils, other derivatives of dicarboxylic acids always leads to a change in the chemical and mechanical characteristics of formed coatings. Thus, the use of chlorinated compounds decreases the combustibility of film forming oligomers, the use of ending anhydride increases the adhesion of the protective layer [3]. Alkyd oligomers are often used as modifiers of other film formers, such as melamine-, carbamide- and phenol-formaldehyde resins, epoxide oligomers, polyurethanes and others. The chemical structure of the oligomer modifier also plays an important role in such systems of film formers. It should be noted that the alkyd resins with ABOA as an acid agent may be used to obtain a modified melamine alkyd resin. During the modification of melamine-formaldehyde oligomers by alkyd resins by mixing them well combined compositions are formed in which at the formation of the first powder coating curing a set of chemical reactions such as the homocondensation of melamine-formaldehyde oligomers, their heterocondensation with alkyd resins (AR) by terminal amino groups of MFO with carboxyl groups, hydroxyl and carboxyl end groups of the polyester, terminal hydroxymethylol and hydroxyl groups (MFO and AR) proceeds [1].

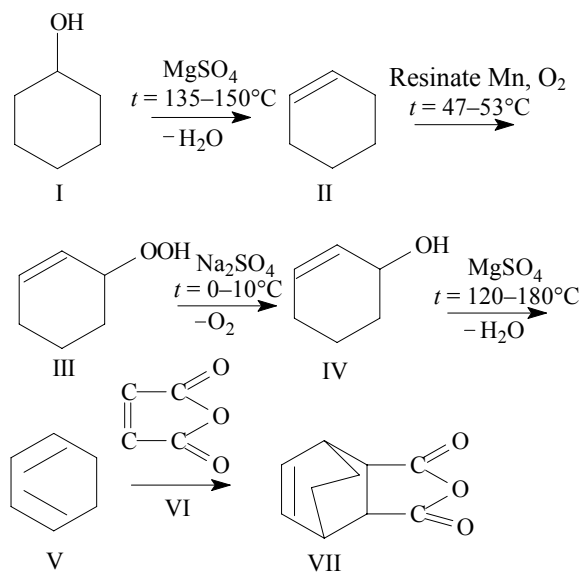
It is known that the degree of homocondensation of MFO is determined by the reactivity of its functional groups (-NH<sub>2</sub>, -CH<sub>2</sub>OH) and by the type of resin, the presence of catalysts, temperature, nature of used solvents. The process of curing can increase the hardness of coatings, their resistance to the action of solvents, but it leads to the decrease of strength at break and adhesion.

Heterocondensation (mutual curing of oligomer macromolecules) provides obtaining of flexible,

chemical- and atmosphere resistant coatings. Thus for the production of coatings with a predetermined set of operational properties the compositions of film forming substances should be highly reactive. It is ensured by a rather high content of amino-, hydroxymethylol, hydroxyl, carboxyl groups in the polymer system and by high unsaturation of acid residues of vegetable oils, in particular by the presence of conjugated double bonds in them. The introduction of the cyclohexane structure with multiple bonds into the bicyclic anhydride system will increase the adhesion of the formed coating to the substrates of different nature.

This article presents the results of studies on the synthesis of alkyd resin modified by two-stage monoglyceride method with the use of bicyclo[2,2,2] oct-5-ene-2,3-dicarboxylic acid anhydride as acylation agent in the polycondensation reaction with polyols, obtaining lacquer coatings and the study of their operational characteristics.

**Main part.** Getting of bicyclo[2,2,2]oct-5-ene-2,3-dicarboxylic acid anhydride was performed by five-step synthesis, using industrially produced cyclohexanol (I) as a starting raw material according to the following scheme (see below).



Cyclohexene(II) with a boiling point of 82–83°C, a density of 0.811–0.814 g/cm<sup>3</sup>,  $n_D^{20} = 1.4450$ –1.4470 was obtained by dehydration of industrially produced cyclohexanol at 135–150°C in the presence of calcinated magnesium sulphate. For this purpose the reactor with a reflux condenser was used. The cyclohexene output was 60 %.

Cyclohexene hydroperoxide was obtained by oxidation of cyclohexene by the following way: in the oxidation reactor equipped with a stirrer, a reflux condenser and a device for the introduction of oxygen, 1,500 ml of purified cyclohexene(II), 3 g of manganese resinate as a catalyst for the oxidation were introduced and oxygen was passed through the solution. Oxidation was performed at 47–53°C to the accumulation of ~40 wt % of cyclohexene hydroperoxide in the mixture(III).

Manganese resinate which was used as a catalyst for the oxidation of cyclohexene was obtained by the interaction of an alkali solution of resin acids contained in resins, with a solution of manganese chloride. Resins in the mass of 10 g was dissolved in 140 ml of 1% sodium hydroxide. The obtained solution was mixed with 42 ml of 50 % solution of manganese chloride. The resulting amorphous precipitate was washed from the alkali to a neutral reaction. The precipitate was extracted, dried at first in air at 20°C, then at 50–60°C.

Cyclohex-2-ene-1-ol(IV) was prepared from cyclohexene hydroperoxide (III) in the reactor equipped with a stirrer and a dropping funnel. In the reactor there were introduced 126 g of crystalline hydrate of sodium sulphate and 1,230 ml of distilled water (to obtain a saturated solution) and slowly were added in drops with vigorous stirring 750 ml of the oxidized reaction mass containing 40 % of cyclohexene hydroperoxide (III). The temperature of the reaction medium was maintained in the range of 0–10°C. When the process was finished (lack of reaction to the hydroperoxide) the reaction mixture was placed in a separatory funnel to separate the hydrocarbon layer from water. The hydrocarbon layer was dried by calcinated magnesium sulphate and then distilled at a residual pressure of 2 mm Hg. Art. Cyclohex-2-ene-1-ol was distilled at 48–50°C.

For the synthesis of cyclohexane-1,3-diene(V) the dehydration reaction of cyclohex-2-ene-1-ol was carried out. In the reactor with a reflux condenser there were introduced 98 g of cyclohex-2-ene-1-ol,  $n_D^{20} = 1.4828$ , 120 g of calcinated magnesium sulphate and heated in an oil bath at 120–180°C. After the distillation of dried by magnesium sulphate product 60g (73%) of cyclohexane-1,3-diene with the boiling temperature of 78.5–79.5°C,  $n_D^{20} = 1.4746$ –1.4755, the density of 0.8435–0.8440 g/cm<sup>3</sup> were isolated.

The condensation of cyclohexane-1,3-diene(V) with maleic anhydride (VI) was performed as fol-

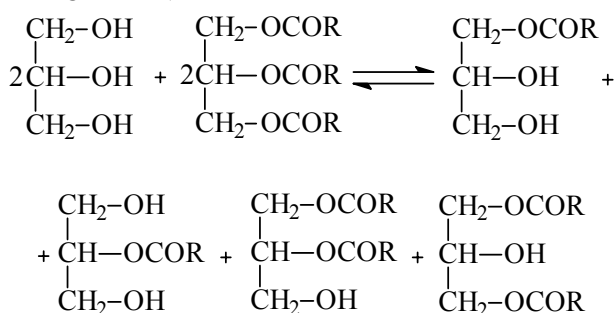
lows: in the reactor equipped with a stirrer, a reflux condenser, a dropping funnel 61.2 g of maleic anhydride dissolved in 300 ml of calcinated benzene was introduced. Then cyclohexane diene (60 ml) was slowly added dropwise from the dropping funnel. The temperature of the reaction medium was maintained at 39–41°C. After the end of the synthesis the solution was cooled, the formed crystals of bicyclo[2,2,2]oct-5-ene-2,3-dicarboxylic acid anhydride were filtered off and recrystallized from benzene-petroleum ether (1 : 1) to get 60 g (58%) ABEA melting at 147–149°C.

For the synthesis of alkyd resin glycerine and pentaerythritol as the alcohol components were used, and as modifying oils flax and sunflower oils were used.

Alkyd resin synthesis conditions varied by temperature process steps, their duration, the presence or absence of catalysts and were monitored under transesterification solubility in ethanol and the condensation step for acid ratios providing solubility of the synthesized oligomer (linear structure). The molecular weight and molecular weight distribution of the synthesized alkyd oligomer on the base of ABEA depend as well as for alkyds based on phthalic anhydride on the method and conditions of synthesis.

Typically, the method of glyceride synthesis of alkyd resins, regardless of the structure of an acid and alcohol component (glycerine or pentaerythritol), of modifying oils (flax or sunflower) is carried out in two stages. The first stage- the transesterification (alcoholysis of vegetable oils) is in the interaction of polyols (glycerine or pentaerythritol) with vegetable oil, including next transformations (Scheme of alcoholysis of oil by glycerine, see below). By varying the parameters of the transesterification stage (temperature, duration, presence of a catalyst) one can regulate the degree of alcoholysis on the content of hydroxyl groups in the taken samples of the oligomer, experimentally determining the hydroxyl number, molecular weight (on the viscosity of the oligomer) and to evaluate the molecular weight distribution[1].

The transesterification stage in this work was carried out in conditions close to production, at the temperature of (245 + (–5))°C for 0.5–2 h using PbO<sub>2</sub> as a catalyst in the inert environment (in the nitrogen flow).



R-the remains of a straight-chain unsaturated and saturated fatty acids.

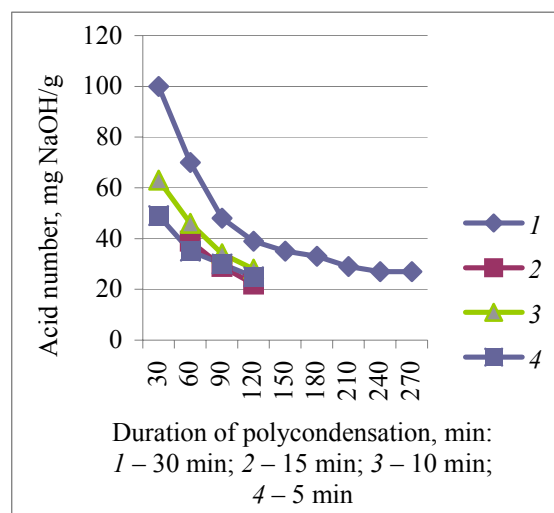
The monitoring of the progress of the process of alcoholysis was performed by the standard method for the esterified sample solubility in ethanol. The control of the solubility of the reaction mixture was exercised 15–20 min after the temperature of the reaction medium achieved 240°C. The end of the stage of the transesterification process was determined by the achievement of the complete solubility of the sample of the reaction mixture in ethanol at a ratio of the reaction mass and ethanol for at least 1 : 10 at 18–20°C. The complete solubility of the sample in ethanol is the proof of the end of the transesterification process. In the conditions of the fulfillment of these studies the distribution of layers of the system oil: glycerine was observed for 25–55 minutes depending on the temperature of the transesterification process and the intensity of stirring of the reaction mixture. During the visual observation of the flow of the stage of alcoholysis of flax or sunflower oil by glycerine it was found that after the indicated time in the analysed system a turbid medium is formed for 1–2 min with the subsequent full mutual dissolution of mixture components in ethanol. However, the system contains not only the mono-, di-, triglycerides, but free glycerine too [1].

In this regard the second stage of the synthesis of alkyd resin after the addition in the reaction medium of calculated amount of bicyclo[2,2,2]oct-5-ene-2,3-dicarboxylic acid anhydride is performed in the system of a complex composition which leads to the formation of the ester oligomers with a broad molecular weight distribution. As shown previously [1], the quantitative formation of oligomers with a high molecular weight is achieved in the reaction mixture, obtained from the products of transesterification with the highest content of  $\alpha$ -hydroxymethyl groups.

The figure shows the results of the study of the polycondensation process of flax oil by glycerine with ABEA to AN = 20 mg NaOH/g depending on the time of the exposure of the transesterificate at the temperature of oil alcoholysis.

It is experimentally established that the exposure of the reaction mixture of the transesterificate over 25 minutes can lead to the gelation at even higher acid numbers of alkyd resin.

Lacquer coatings were applied by the applicator from solutions. The curing was carried out in the thermostat. After the curing the thickness of the coatings was 20–30 microns. The coating hardness was determined in accordance with GOST 5233, the flexural elasticity according to GOST 6806, the adhesion according to GOST 15140 and the impact resistance according to GOST 4765. The acid number of synthesized alkyd oligomers was determined by the method [4].



Effects of time of the exposure of the reaction products of transesterification of flaxseed oil by glycerine on the change of the acid number and the duration of the second stage of the alkyd oligomer synthesis based on ABEA until the acid number of 20 mg NaOH/g

Table 1 shows the composition and the characteristics of lacquer coatings. As shown in Table 1 the hardness of lacquer coatings in dependence of the type of the alcohol component, of the fat degree of alkyd resin based on bicyclo[2,2,2]oct-5-ene-2,3 dicarboxylic acid anhydride is 0.21–0.30 rel.u., that in all cases is greater than the meaning of this characteristic for alkyd resins based on phthalic anhydride, glycerine and linseed oil with a fat degree of 30%. The adhesion for all samples of alkyd resins based on ABEA is higher compared with sample 6, in which the acid component is the phthalic anhydride. The moisture resistance of alkyd resins based on ABEA is 200 hours at 20°C and about 10 hours at 60°C, while this index for glyptal resins is 150 and 3 hours respectively.

The experiments on thermal ageing of lacquer coatings at 180°C in air during 60 hours showed that under these conditions visible changes of all coatings are not observed. The impact resistance for all samples is at least 80 cm at a mass of 1 kg of cargo, the flexural strength is 1 mm, the heat resistance at 150°C is 18 hours.

The light resistance of lacquer coatings was determined by the change of the appearance and the indicators of the hardness and elasticity of coatings before and after UV-irradiation.

Steel plates coated and dried for the perfect coating were irradiated in the chamber by the mercury-quartz lamp PRK-2 at a distance of 30 cm at 30°C for 120 hours.

The alkyd resin composition and physical and mechanical characteristics of lacquer coatings before and after UV-irradiation are shown in Table 2. The flexural strength of all samples before and after UV-irradiation for 120 hours is 1 mm.

Table 1

**Composition and characteristics of lacquer coatings**

Sample number	Resin composition		Coating thickness, mm	Hardness, c. u.	Moisture resistance		Adhesion score	Rust on an iron plate at 20°C in water, days
	Alcoholic component	Fat content, %			at 20°C, h	at 60°C, h		
1	G	30	0.04	0.30	200 hours without any visible changes	5.0	0	>60
2	G	40	0.03	0.29		4.0	0	>60
3	G	50	0.05	0.25		4.5	0	>60
4	PE	60	0.06	0.29		9.5	0	>50
5	PE	60	0.05	0.21		10	0	>65
6*	G	30	0.05	0.18	150 hours without any visible changes	3.0	1	>48

\*Synthesis of alkyd resins on the base of phthalic anhydride, glycerine and linseed oil.

Table 2

**Alkyd resin compositions and physical and mechanical characteristics of lacquer coatings before and after UV-irradiation**

Resin composition			Physical and mechanical characteristics of lacquer coatings	
Acid component	Alcoholic component	Fat content, %	Hardness before irradiation, c. u.	Hardness after irradiation for 20 hours, c. u.
ABEA	G	50	0.25	0.32
ABEA	PE	60	0.21	0.30
ABEA	PE	30	0.24	0.26
Phthalic anhydride	G	30	0.18	0.34

Table 3

**Dependence of the properties of lacquer coatings on the exposure time of the transesterificate (glycerine-linseed oil – ABEA) and curing**

Properties of the coatings, curing conditions	Exposure time of transesterificate after the solubility in ethanol, min				
	5	8	10	15	20
Adhesion, score					
80°C, 60 min	0	0	0	0	0
110°C, 20 min	0	0	0	0	0
135°C, 30 min	0	0	0	0	0
Impact resistance, kgf·cm					
80°C, 60 min	60	90	110	60	40
110°C, 20 min	45	60	90	55	95
135°C, 30 min	40	50	70	60	70
Hardness, rel. u.					
80°C, 60 min	0.20	0.35	0.25	0.16	0.10
110°C, 20 min	0.25	0.50	0.30	0.25	0.20
135°C, 30 min	0.30	0.45	0.35	0.30	0.55

Table 2 presents the data about the composition of alkyd resins and physical and mechanical characteristics of lacquer coatings before and after UV-irradiation. The analysis of the data in Table 2 shows a higher resistance to the UV-irradiation of coatings based on alkyd resins, synthesized with the use of bicyclic dicarboxylic acid anhydride with a multiple bond in the six-membered ring as compared with the stability to UV-irradiation based on the industrially produced glyptal resin.

The properties of lacquer coatings depending on the exposure time of the transesterificate (glycerine-linseed oil – ABEA) and curing conditions are shown in Table 3. As shown in Table 3, the best

mechanical characteristics of lacquer coatings based on alkyd resins, synthesized using ABEA are obtained at the exposure of the transesterificate in the reactor for 8–10 minutes.

Thus, to obtain the optimum properties of coatings formed from alkyd resins synthesized using ABEA, you must consider not only the moment of disappearance of the interface of oil and glycerine, but the time of the exposure of the transesterificate towards alcoholysis, the qualitative and quantitative composition of products of alcoholysis and the duration of the polycondensation process of the transesterificate with ABEA and the characteristics of derived resins in accordance with the acid number.

In addition it was found that the chemical modification of alkyd resins (GF, PF) of the replacement of phthalic anhydride on bicycle [2,2,2]oct-5-ene-2,3 dicarboxylic acid anhydride increases the hardness, the resistance, the adhesion of coatings formed on the steel substrates. To ensure the desired properties of formed coatings it is necessary to follow the technological parameters of the process of the glyceride method of the alkyd oligomer synthesis on the base of ABEA both during the transesterification process with the fixed transesterification exposure from the moment of disappearance of the interface of oil and glycerin at least 8–10 minutes and the polycondensation stage, preventing the transition of a linear oligomer in a three-dimensional cross-linked product.

To investigate the possibility of modifying the synthesized alkyd oligomer by petro polymeric resin was also of interest in this work. For this purpose the petro polymeric lacquer resin of grade B (TU 38.10918-79) with a softening point of 91°C and the mass fraction of solids of 99.86 % was used.

Petropolymeric resins (PPR) are products of polymerization of petrochemicals containing mostly unsaturated aromatic and olefinic hydrocarbons.

These are thermoplastic polymers with a softening temperature up to 150°C, they can be used as independent film formers. PPR are cheap and available polymers which have a number of valuable properties with high acid-, alkali- and water-resistance, good solubility in aromatic and naphthene hydrocarbons, higher alcohols[1].

They have unlimited compatibility with oils and alkyd oilomers. In this context it seemed appropriate to use them as modifying film formers in complexes with an alkyd resin synthesized on the base of the bicyclo -dicarboxylic acid anhydride, containing a multiple bond in the cycle capable to the film forming process at the formation of coating of hot curing to form chemical bonds with PPR and at the expense of the reinforcing structure in the system to ensure the advancement of the complex of operational characteristics of the polymer protective layer.

Binary mixtures of PPR and an alkyd oligomer were prepared at different ratios of the solutions of initial oligomers with an interval of 10%, using a solution of the PPR in the solvent with a mass fraction of 50% solids.

In the process of heating of samples initially transparent films were becoming turbid. The turbidity increased with an increase of the time of heating as the solvent evaporated. This is probably due to changes in the phase composition of the mixture. The system is homogeneous and transparent at the 50% mass concentration of oligomers.

During the process of curing when the solvent evaporates the concentration of the mixture of oligomers increases and the system goes over into the

heterogeneous region. This allows to suppose that the initial binary mixture of oligomers has limited compatibility and with the change of their relationship the fuse separation of the system takes place.

During the study of the properties of the mixture of film forming agents it was established that within the compatibility of PPR and synthesized oligomers the properties of the coatings based on the compositions of binary systems are improved compared to non-modified alkyd resin samples (Table 4).

Table 4

**Mechanical characteristics of films of film formers**

Concentration of PPR in the mixture of a film form	Film impact resistance, sm	Film elasticity in bending, mm	Adhesion, score	Water resistance in 2 months
0	55	1	1	Unchanged
5	60	1	0	Unchanged
10	60	1	0	Unchanged
15	60	1	1	Unchanged
20	60	1	1	Unchanged
25	40	3	1	The film is slightly turbid
50	0	6	2	The film becomes turbid

**Conclusion.** Thus, on the basis of the experimental results on the synthesis of alkyd resins with the use of bicycle [2,2,2] oct-5-ene-2,3 dicarboxylic acid anhydride, it can be affirmed that a full or partial replacement of phthalic anhydride on ABEA when obtaining alkyd resins of various degree of fat and the structure of the alcohol component is quite possible, especially since the production of ABEA in Belarus can be carried out within the program of a little tonnage chemistry of “Azot”(Grodno) where cyclohexanol, the starting material for the synthesis of ABEA is produced.

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### CURING OF EPOXYDIANE RESINS BY MODIFIED HARDENER OF AMINE TYPE

The paper presents the results of a comprehensive study of changes in the properties of film-forming compositions based on epoxydiane oligomer. Curing was carried out by a modified hardener. The degree of structurization changes depending on the amount of the hardener. The effect of time-temperature conditions, ratio of initial oligomers, and nature of the solvent on the process of epoxydiane resin curing by modified polyamide was determined.

**Introduction.** Epoxy oligomers are widely used in industry, paintwork material production including. It is known that manufacture of a large assortment of paintwork materials based on epoxydiane oligomers is much conditioned by modification.

We carried out a comprehensive investigation of changes in the properties of film-forming compositions based on epoxydiane oligomer E-41sol (TU 6-10-1316-84) cured by a cross-linking agent of hardener N 4 – solution of polyamide resin. The hardener modifier was oligomer polyamine of aromatic structure with a system of conjugated bonds – oligoaminophenylene (OAP). At increase of the modifier content under the conditions of the coating curing, the system of epoxy oligomer reveals increase of the degree of structurization which is defined by a numerical ratio of the composition components resulting in increase of the layer (coating) adhesion which changes along the curve with the maximum.

The effect of time – temperature conditions, ratio of initial oligomers and nature of the solvent on the process of epoxydiane resin curing by modified polyamide was determined. A considerable effect of the structurization process in epoxy-polyamide-amine compositions on properties of coatings based on these compositions was shown.

It is also known that one of effective ways (techniques) of modifying film-forming oligomers is a combination of film-formers with various functional groups. It often appears that in case of combining various film-formers a corresponding effect is achieved regardless of the fact whether they form a real solution, mechanical mix or micro-heterogeneous system. Since real compatibility of film-former polymers is limited in the majority of cases micro-heterogeneous two-phase systems serve as modified compositions [1]. Epoxy resins, particularly epoxydiane ones, can't be used without special reagents-hardeners. The exception are high-molecular phenoxy resins with the weight 10–150 thousand, and some modified epoxy ethers and epoxy alkyds (resin E-30). In other cases hardeners must be used in compositions of epoxy paintwork materials. This leads to the necessity to develop two-package systems.

Though sometimes the mixture of resins and hardeners possesses limited viability researchers face the possibility to create (develop) new materials with specified properties by varying the composition of the hardener. It is the choice of the hardener that is the determining factor for providing the required technological and performance characteristics of paintwork coatings based on epoxy resins [2].

It should be noted that epoxy resins are of significance for production of anticorrosion paintwork materials. It is explained by a set of unique properties of these film-formers:

- low viscosity, especially in combination with reactive diluents, plasticizers and hardeners;
- ability to hardening at ambient temperature, and in the presence of a catalyst – at lower temperatures;
- minimal shrinkage in the process of hardening allowing for a low level of inherent tension in coatings based on these resins;
- perfect adhesion of epoxy coatings to various materials (metals, concrete, glass, stone, etc.) in combination with a set of high physico-mechanical properties;
- sufficient anticorrosion characteristics because their molecules contain epoxy, hydroxyl, ether groups and aromatic rings [2].

In some cases, however, consumers aren't completely satisfied and demand epoxy film-formers be of better quality. That's why investigations oriented to improvement of performance characteristics of coatings based on these materials are still vital.

The present paper is a continuation of such (similar) investigations. It focuses on the study of the effect of the modifying impact of the oligomer polyamine compound (OAP) on the hardening process of epoxydiane resin E-41sol by the solution of the polyamide hardener modified by OAP so as to verify the possibility of purposeful control of interphase hardness. The paper also investigates the impact of thermo-resistant oligomeric polyamine of aromatic structure (OAP) on the change of physico-mechanical properties of the component mixes in the process of hardening and on the dependence