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M. V. Zhuravleva, PhD student (BSTU);**E. T. Krutko**, D. Sc. (Engineering), professor (BSTU);**T. A. Zharskaya**, PhD (Engineering), assistant professor (BSTU)**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.

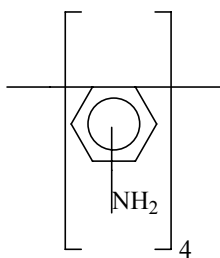
The present paper is a continuation of such (similar) investigations. It focuses on the study of the effect of the modifying impact of the oligomer polyamine compound (OAP) on the hardening process of epoxydiane resin E-41sol by the solution of the polyamide hardener modified by OAP so as to verify the 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

of properties of hardened coatings on the volume of the modifier injected.

Main part. The object of investigation was industrial resin E-41 in solution (E-41 sol) (TU-6-10-607-78). This resin is a solution of resin E-41 with mass share (66 ± 2) % in the mixture of xylene (State Standard 9410-78, State Standard 9949-76) with acetone (state standard 2768-84) in ratio 4 : 3 by mass. Resin E-41sol is used in paintwork production to obtain materials for formation of coatings for various applications. Density of resin E-41sol is equal to $1.03\text{--}1.06\text{ g/cm}^3$. It is referred to mean-molecular (molecular weight is 900–2,000) resins. It is a product of copolycondensation of low molecular resin E-40 with diphenylolpropane. This structural formula of the oligomer is given further.

Due to high reactive ability of epoxy and, to a less extent, hydroxyl groups monomeric, oligomeric and polymeric compounds of various classes can be used as the hardener in epoxy resin. By the mechanism of polyaddition epoxy resins are hardened by primary and secondary, di- and polyamines, multibased acids and their anhydrides, as well as by phenol-, urea- and melamine-formaldehyde resins; by the mechanism of ion polymerization – by tertiary amines, aminophenols, their salts, acids Lewis and their complexes with bases.

A modified polyamide dissolved in the mixture of organic solvents (modified hardener N 4) was used as the hardener for epoxydiane resin E-41sol. The modifying component of the hardener was oligomeric polyamine of aromatic structure with a polyconjugated system of chemical bonds in the macromolecules – oligoamino-phenylene (OAP) formula:



The synthesis of OAP was made by condensation of *n*-phenylenediamine in the nitrogen current in the presence of the catalytic amount of *n*-toluene-sulfur acid in melt in the following way: *n*-amino-phenol (nAP) and *n*-toluenesulfur acid in the amount of 7 wt % of the mass of nAP were loaded into a four-neck flask supplied with a stirrer, thermometer, reverse refrigerator, and capillary tube for injecting nitrogen. At temperature $230\text{--}240^\circ\text{C}$ the reaction mix was cured for 4 hours. Then the reaction mix was cooled to 200°C ; dimethylformamide was carefully added to obtain 50%-solution which was then cooled to ambient temperature and precipitated

with distilled water. The sediment was rinsed/washed with 10% aqueous ammonia solution and distilled water, dried and extracted with diethyl ether in the unit Soxhlet for purifying oligoaminophenylene OAP from *n*-toluene-sulfur acid and unreacted diamine. The obtained product was a powder of black colour.

Fractionation of paraoligoaminophenylene was carried out by extraction of the purified oligomer in the unit Soxhlet: at first fraction 1 (nOAP-1), then by dimethylformamide – fraction 2 (nOAP-2), for 24–26 hours with subsequent distillation of the solvent in a rotation evaporator. The obtained products were dried at ambient temperature in the vacuum.

Determination of the molecular weight of oligoaminophenylene was performed by the method of cryoscopy based on the decrease of the solvent freezing temperature when it dissolves the substance under analysis. This method provides reproducible results at studying oligomers with the molecular weight not exceeding 500, but in general the sensitivity of the method is limited by the molecular weight 2000–2500 [2].

Formamide and formic acid were used as solvents. The formamide was dried by calcium hydride and distilled in the vacuum. The formic acid with the 99.7 % content of the main substance was dried by non-aqueous copper sulfate and distilled in the vacuum at ambient temperature. The obtained values of melting temperature for the formic acid was 8.1°C , and for the formamide – 2.5°C .

Determination of the molecular weight of oligomer was performed in accordance with the technique [4].

The content of amine groups in oligoaminophenylene was determined by the method of potential metric titration in a laboratory ion-meter with a glass-calomel system of electrodes.

The mixture of DMP: methylethylketone (1 : 1) was used as an OAP solvent; 0.1 n. solution of perchloric acid HClO_4 in methylethylketone was used as a titration vehicle. Drying (dewatering) and purification of the methylethylketone from acid admixtures was performed by shaking it with non-aqueous potassium carbonate with subsequent distillation. The titre of HCl solution was visually established by potassium biphthalate in the presence of a crystal violet indicator (marker).

The error of the aminogroups content was 3% of the definition.

Film-forming compositions were prepared in the following way: hardener N 4 (polyamide resin in the solvent) containing the modifier OAP in the volume 0.1–1.0 wt % from the weight of the dry sediment was injected into the epoxydiane resin E-41sol, and then the mixture (mix) was agitated to a uniform state. The obtained varnish mixes were

used to cast films (coatings) on steel and glass substrates. Curing of the coatings was performed by heating the film-forming compositions in a thermochamber at 100, 110, 120°C for 60–220 min.

The adhesion strength of the formed coatings was defined by the standard technique in accordance with ISO 2409 and State Standard 15140-78 by the method of screen incision with the inverse (reverse) blow. The essence of the method is as follows: screen incisions (cuts) are marked on the coating with the help of the unit “Adhesion meter PH”, then visual assessment of the coating screen incisions after a blow on the reverse side of the plate in the place of the incisions is made (carried out) with the help of the unit “Udar-Tester”. This method is assigned for defining adhesion strength of highly elastic coatings.

The impact strength of the coating samples was evaluated with the help of the unit “Udar-Tester” in accordance with ISO 6272 and State Standard 4765-73. The method of determining impact strength of the film is based on instantaneous deformation of a metallic plate with a paintwork coating in a free fall of the load on the sample and is realized with the help of the unit “Udar-Tester” which is assigned for control of impact strength of polymer, powdery and paintwork coatings.

The flexural strength of the coatings was determined with the help of a unit consisting of a stanchion (upright) with casing and a set of cylinders of various diameters (ISO 1519, State Standard 6806-73). The sample with a coating under analysis is slowly bent around the cylinders beginning with larger diameters to angle 180°. On one of the cylinder diameters the coating either cracks, tears or peels. In this case it is considered that the coating possesses the elasticity of the preceding diameter of the tested cylinder of the unit where it doesn't break. The reading is made in the radii of bending in millimeters.

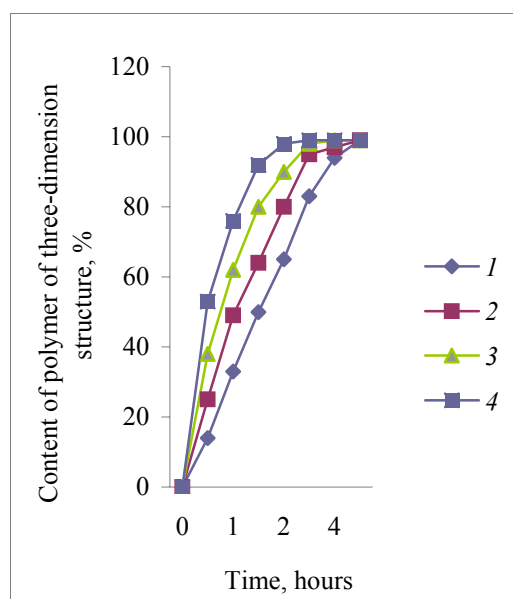
Hardness is a very important property (characteristics) of paintwork coatings. This parameter was defined by a pendulum device (ISO 1522). The essence of the method lies in defining the time of the pendulum fading (the number of oscillations) at its contact with the paintwork coating.

As it is shown in the paper [5], in studying reactivity of some oligomer polyamines in reactions of formation of polyaminoamide acids (due to lack of an excessive bend on the heat curves of reactions of polyacylation) under the conditions of the experiment there are mainly formed macromolecules of polyamine-amide acids of linear structure. But in case of their usage in epoxydiane oligomers (which contain active end epoxy and hydroxyl groups capable to react with NH₂-groups of oligoaminophenylene) in the process of curing the screen structure is formed in addition to the poly-

amide hardener with NH₂-groups in the polymer coating. The results of the IR-spectroscopy investigations provide information on the flow rate of NH₂-groups in subsequent transformations.

The IR-spectra of the film samples obtained on glass substrates were made by the device FI-IR (IK “Furye-spectrometer of the firm “Thermo Nicolet”, USA).

The figure presents the results of the study of the process of formation of a three-dimension structure in the system of an epoxydiane film-former in the presence of polyamide hardener N 4 modified by oligoaminophenylene on the basis of the change of the content of the undissolved polymer of screen structure in the course of curing.



Kinetics of epoxydiane resin E-41sol curing with various contents of modifier OAP (wt %) at temperature 100°C

The figure indicates that in curing the ED composition by polyamide, modified by 0.1–1.0 mol. % oligoaminophenylene, a polymer coating layer with the maximally high degree of hardness is achieved in 2.5–3 hours, and in case of an unmodified hardener – only in 4 hours at temperature 100°C.

Probably, the use of the polyamide modified by oligomer polyamine-phenylene as a hardener for epoxydiane resin E-41sol allows (in conditions of coating curing) to form, in the system of polymer, a tighter cross-linked structure than when using an unmodified hardener. The degree of structurization of the structure is determined by a quantitative proportion of the components.

Since epoxy oligomers can react with the aminogroups of the polyamide resin (hardener) even at the stage of coating formation, they don't practically participate in formation of adhesion links

with the metallic surface of the articles under protection. Hydroxyl groups of epoxy oligomer form hydraulically unstable links of the coating and the surface of the metal. The modifying additive of oligoaminophenylene contains adhesive active functional groups – NH₂ and aromatic conjugated fragments of the oligomer which, on the one hand, possess adsorption reactivity in relation to metals and their oxides [6], and, on the other, are capable to react with epoxy cycles of the epoxydiane oligomer. Besides this additive forms a screen structure. The thickness of the screen of the coating three-dimension structure is defined by the quantitative volume of the film-forming composition ingredients with their optimal content in the composition.

Table 1 presents the change of the performance properties of the coatings formed from the obtained epoxydiane compositions hardened by modified 0.5 wt % OAP polyamide at 100, 110, 120°C, depending on the duration of temperature impact.

Table 1 indicates that at temperature rise of curing epoxydiane resins with polyamide hardener N 4, modified by 0.5 wt % OAP, there occurs in-

crease of hardness, adhesion strength to steel substrates (in heating the coatings at 100°C for 140–160 min); the impact strength of the coating in the conditions of curing at 100°C during 140–200 min increases almost twice.

Since steel constructions and devices operate not only indoors but are often exposed to the impact of external aggressive aqueous media effecting the surface of the metal, it seemed reasonable to evaluate the property of water resistance and water absorption of protective layers of the coatings formed from the developed film-forming imide-containing epoxydiane compositions.

In conformity with increase of adhesion to steel, other parameters of the coating are also changing. For example, water resistance increases by 2.2 times, water absorption decreases from 0.60 to 0.35%.

Table 2 indicates that the best results on water resistance, water absorption ability are obtained for the composition in the given quantitative proportions, considerably exceeding this parameter for the system.

Table 1

Physico-mechanical properties of coatings based on epoxydiane resin E-41sol, cured by polyamide (hardener N 4), modified by 0.5 wt % OAP

Curing conditions		Hardness, %	Adhesion to steel, point	Impact strength, sm, no more
Temperature °C	Duration, min			
100	60	60	1	9
	80	65	1	10
	100	70	1	9
	120	70	1	9
	140	75	1	18
	160	75	1	18
	180	75	0	18
	200	65	0	10
	220	60	1	7
110	60	70	1	8
	80	75	1	8
	100	80	0	15
	120	85	0	15
	140	85	0	15
	160	85	1	10
	180	70	1	10
	200	60	1	9
	220	60	2	7
120	60	71	1	5
	80	74	1	5
	100	86	0	8
	120	70	0	9
	140	69	2	6
	160	73	2	3
	180	70	3	3
	200	69	4	2
	220	65	4	1

Table 2
Water resistance and water absorption
of the obtained coatings

Parameter	Index			Compo- sition
	OAP content in the hardener composition, wt % on the dry sediment			
	0.1	0.5	1.0	
Water resistance at 100°C, h	20	21	39.75	18.3
Water absorption at the equilib- rium, %	0.4	0.55	0.35	0.6

Thus, water resistance was determined by visual observation of changes in the outer appearance of the protective coating and occurrence of under-film corrosion on the steel substrates in the process of exposing steel plates with a varnish protective layer in running water under ordinary conditions and at 100°C (boiling).

The method of determining water absorption is based on the ability of the varnish coating to absorb water. Water absorption is evaluated by the volume of the water absorbed by the film at the given temperature; it is expressed in % or weight of the absorbed water in relation to the film weight unit.

Water absorption was determined by evaluation of absorption capacity of the varnish coating in relation to water. The samples of unadhered (taken from the substrates) films were weighed and placed into the aqueous medium. These films were kept there for a long time (till the uniformity of the mix); and then on the basis of the difference in the weight of the film samples (samples with maximal water absorption and the initial ones) we defined the amount of the combined water expressing it in % in relation to the unit of the film weight of the epoxydiane composite.

Development of the screen structure in the presence of polyamidoacids increases because PAA adds carboxyl and amide active centers to the system epoxydiane – polyamine. Due to the mobile protons of PAA carboxamide fragments and the hardener these centers don't only enhance effective chemical reactions but are conductive to the autocatalysis of a number of other competitive reactions occurring in the system. Besides there may be other reactions in the PAA molecules: imidization, destruction, hydrolysis, decarboxylation which proceed under the impact of temperature – time conditions and discharged cyclic water in the process of high-temperature treatment of protection layers at coating formation [4]. These transformations generate a larger number of functional groups enhancing structurization in the coating and coating adhesion to the substrate.

As a result, these processes lead to more effective structurization in the system of the developed

oligomer composition, formation of a tighter cross-linked screen structure of the coating and improvement of its adhesion characteristics. Obviously, the use of a modifier for the hardener-epoxy composition allows (in the conditions of curing) to form a screen structure in the protection layer, the degree of structurization is defined by the quantitative proportion of components in the composition.

Conclusion. Creation of composite materials with a specified complex of physico-mechanical properties is one of the most essential directions in development and production of composite materials. The aim of the present work was creation of composite materials based on epoxydiane resins. Evaluation of paintwork material quality is of great importance in their production and application.

Thus, in curing epoxydiane resins by hardener N 4 (polyamide resin in solution), modified by oligoaminophenylene we can both accelerate the process of hardening the coating based of these oligomers, and greatly improve protective and adhesive properties of coatings on metallic surfaces.

Application of this composition at enterprises of ship- and machine-building industry and aerospace engineering will help to increase durability of the obtained coatings and that of articles and devices coated with this composition, thus enhancing their competitiveness.

As a result of our investigation we synthesized new film-forming imide-containing compositions with improved adhesion properties, higher hardness, impact strength, moisture- and water-resistance.

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