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OLIGOAMINOIMIDOPHENYLENE, EFFECTIVE MODIFIER FOR MELAMINALKYD VARNISH

The present article deals with the development and study of new coatings based on industrially produced melamine-alkyd varnish of improved performance characteristics. It describes the synthesis of a dis-oligomeric amineimido modifier which is soluble in ethyl cellosolve and polar aprotic solvent, various formulations of varnish composition being also investigated. The physical-mechanical properties of coatings prepared from the compositions involved have been analyzed. Due to the formation of additional network structure, the introduction of the proposed modifier allows to increase the hardness of coatings, their impact and water resistance, as well as to improve adhesion while maintaining coating elasticity. The composition developed contributes to a significant increase in the life of the coating for automobiles, buses, trolley buses, agricultural and other machinery and steel structures.

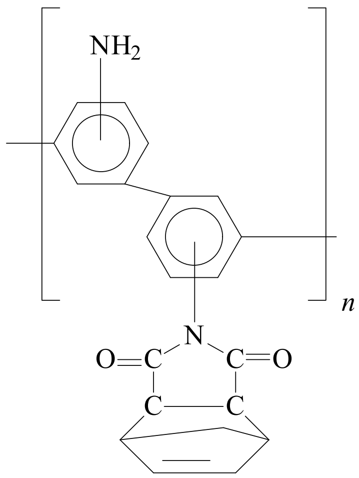
Key words: melamine-alkyd resin modification, coating, adhesion, hardness, water resistance, strength.

Introduction. Melamine-alkyd resins find wide application as components of paint-and-varnish materials suitable for preparing protective coatings for various purposes. However, they have insufficient resistance to moisture, acids and alkalis.

One way of improving the properties of film formers for paint-and-varnish materials is the use of monomers of different chemical structure during their synthesis. However, more effective and accessible method of achieving maximum conformity of theproperties of the coatings concerned to the requirements of specific applications, i.e. developing the necessary properties in them, is the addition of small amounts of modifying agents into the composition of commercially available polymer film formers. Efficiency of the method involved is shown, for example, in [1, 2].

Main part. The present work has been aimed atthe development and study of new film materials based on melamine-alkyd varnish, their protective properties being improved by its modification. The main object of the study involved was ML-0136 (TS 6-10-1392-78 with am. No. 1–4, and add. STP 07-98) melamine-alkyd varnishproduced at the JSC "Lakokraska" in Lida. ML-0136 is glyptal polyester modified with dehydrated castor oil mixed with K-421-02 (30 wt %), highlybutanatedmelamine-formaldehyde resin in the form of solution in the mixture of solvent and white spirit (in the ratio of 1 : 1). The main characteristics of the varnish used in the research are conditional viscosity of 90–150 s measured with VZ-4 type viscometer at the temperature of (20.0 ± 0.5)°C; non-volatiles mass fraction of 50%; acid number of 10 mg KOH/g of the varnish; varnish film hardness measured with a TML-type pendulum device (pendulum A) of 0.3 rel. units.

Oligoaminobenzenesulfamidophenylene (OAIF) in the amount of 0.1–1.0% (n = 2–3) was used as the modifier:



Synthesis of oligoaminophenylene from *p*-phenylene-diamine (OAF) was performed in nitrogen flow in the presence of *p*-methyl-benzene sulphonic acid acting as a catalyst, an advanced technique [3] being applied.

p-Phenylene-diamine and 7 wt % *p*-methylbenzene sulphonic acid were poured into a four-throat flask equipped with an agitator, thermometer, reflux condenser and capillary for nitrogen input. After reaching the temperature of 230–240°C the reaction was performed during 4 h. Then the reaction mass was cooled to 200°C, and DMFA was carefully added to obtain 50% solution which after cooling to room temperature was precipitated with distilled water. The precipitate was washed with 10% aqueous solution of ammonia, distilled water, dried and extracted with diethyl ether in Soxhlet device to clean *p*-OAF from *p*-methylbenzene sulphonic acid and the uncombined diamine. The compoundsobtained are powdery (*p*-OAF) products from dark brown to black in color, their yield being 70–80%.

The content of amino groups in OAF was determined through potentiometric titration by using I-130M laboratory ionometer with glass-calomel electrode system [4]. As the solvent for OAF, mixture of DMFA : methyl-ethyl ketone in the ratio of 1 : 1 was used, 0.1 m solution of perchloric acid, $HClO_4$, in methyl-ethyl ketone being employed as filtrating solution. Methyl-ethyl ketone drying as well as refining from acidic admixtures were performed by shaking it with anhydrous potassium carbonate, followed by distillation. The titer of $HClO_4$ solution was determined by potassium biphthalate in the presence of crystal violet indicator.

The titration continued until the constant potential was established, control test being simultaneously performed. The content of amino groups (%) was calculated by the formula

$$[\mathrm{NH_2}],\ \% = \frac{(V_1 - V_2)\cdot 0{,}0016 \cdot K \cdot 100}{m},$$

where V_1 and V_2 are the amounts of acid used for titration of the working and reference solutions, respectively, in ml; m is weighed sample, in g; 0.0016 is the mass of the amino groups, corresponding to 0.1 normal solution of acid, and K is the titer of 0.1 normal solution of perchloric acid.

The error in determining the amino group content is 3%.

Fig. 1 shows the titration curve of OAF solution in the mixture of dimethyl-formamide : methyl-ethyl ketone in the ratio of 1 : 1 by 0.1 M solution of perchloric acid in methyl-ethyl ketone. The curve has two kinks corresponding to separate neutralization of two types of amino groups in the oligomer. The second kink is less pronounced, that may be due to the nature of the oligomer that is a mixture of individual compounds. The number of amino groups in OAF that is determined by the amount of $HClO_4$ used for titration of the total number of amino groups (the second kink of the titration curve) is 21% of OAF weight, which when calculating the molecular mass determined by the cryoscopic analyses, corresponds to three amino groups.

OAIF was obtained using two-stage method by acylation of *p*-OAF with anhydride of bicyclo[2,2,1]-5-hepten-2,3-dicarboxylic acid with subsequent chemical imidization, using the developed mixture composed of acetic anhydride (99.5%) and (benzimidazol-2-yl-thio)-*o*-phenylene-borate (0.5%). The proposed composition of the imidizating mixture makes it possible to increase the yield of the final product and significantly reduce the time of chemical imidization.

Anhydride of bicyclo[2,2,1]-5-hepten-2,3-dicarboxylic acid was gradually added to solution of *p*-OAF in dimethyl-formamide with stirring. After 2 h stirring at 20–25°C imidizating mixture was added to thesolution of amino acid formed. The duration of imidization at 55°C was 107 min. After the reaction 50% acetic acid was added to the mixture obtained, its amount being twofold that of acetic anhydride. The resulting mixture was placed in ice-cold distilled water, the precipitate formed was filtered off, washed with water and isopropyl alcohol and dried in vacuum at 20°C till obtaining constant weight, acid value of 4.1 mg KOH/g. OAIF yield is 93.3%.

Imide-containing melamine-alkyd composition was obtained by adding OAIF modifier as its 10% solution in dimethyl-formamide into commercial ML-0136 varnish, followed by stirring the components till producing homogeneous mass. Such varnish is capable of curing upon being heated with the formation of three dimensional products. After curing the composition deposited on steel and glass base by pneumatic spraying in high voltage electric field or manually by casting or applying brush or roller, forms transparent solid film. The film obtained has high hardness, good adhesion and contributes to increased resistance of metal surfaces to water due to the components providing barrier and adhesion mechanismof protectivenature in the coating in the presence of multifunctional OAIF modifier (containing active amino group that prevents corrosion of metal surface, and the imide cycle with the bond of non-limited reactivity) [5]. The modifier also increases thermal stability of the polymer coating protective layer as a whole, thanks to the combination of poly-interfaced aromatic frame of oligophenylene and imide cycles. The composition is cured for 30 min at 130°C.

The adhesion strength of the coatings formed was determined by standard technique in accordance with ISO 2409 and GOST 15140–78 by cross-cut test method with back impact.

The method consists in forming cross cuts on the finished coating by using “PH Adhesimeter” device and visual evaluation of the coating lattice after impacton the opposite side of the plate in the place of cross cuts done by using “Impact-Tester” device. The method is intended for determining the adhesion of high-elasticity coatings.

Impact strength of coatings studied was determined using “Impact –Tester” device in accordance with ISO 6272 standard and GOST 4765–73. Method of determining impact strength of films is based on the instantaneous deformation of the metal plate with paint-and-varnish coating at the free fall of the load onto the sample and is realized with the help of “Impact-Tester” device which is designed to control the impact strength of polymer, powder and paint-and-varnish coatings.

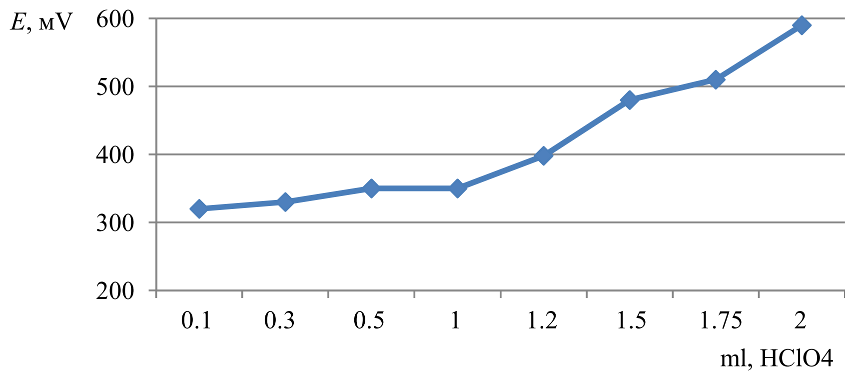


Fig. 1. Curve of potentiometric titration of OAF solution in the mixture of DMFA: methyl-ethyl ketone in the ratio of 1 : 1 with 0.1 M solution of perchloric acid in methyl-ethyl-ketone

Flexural resilience of the coating is determined in accordance with ISO 1519 standard and GOST 6806–73, using a device that consists of a rack with fastening and a set of cylinders of different diameter. To perform testing the sample with the coating to be studied is slowly bent around the cylinders mentioned at the angle of 180° beginning with larger diameters. On one of the cylinders the coating either cracks or breaks or peels off. In this case it is believed that the coating has the elasticity characteristic of the previous diameter of the test cylinder device where it is not destroyed. Reading is in flexure radii and is expressed in millimeters.

An important characteristic of paint-and-varnish coatings is hardness. It was determined according to ISO 1522 standard by using the pendulum device. The method consists in determining the decay time (number of oscillations) of the pendulum at its contact with the paint-and-varnish coating.

Due to the fact that steel constructions and devices are exploited not only internally, but also in the external environment often acting aggressively on the surface of the metal, for example, in water, it has been found expedient to assess the protective properties of the coatings obtained from the developed film-forming imido-compositions during their operation in an aqueous medium (i.e. water-resistance). The results of paint-and-varnish coatings properties study are given in the table.

The kinetics of coating curing was determined through changes in their hardness and in the content of the sol- and gel-fraction in the coating system in time by samples extraction in Soxhlet device, using standard technique.

Fig. 2 presents experimental data obtained in studying the curing kinetics of coatings prepared from the non-modified resin and modified compositions by measuring their relative hardness during curing at the temperature of 130°C. Investigations aimed at the assessment of the sol- and gel-fraction in the cured samples showed that with the addition of 0.1–1.0 wt % of OAIF into ML-0136 melamine-alkyd resin, the gel fraction increases as compared with that in non-modified sample, the maximum increase with the addition of 1% modifier being 99.81%.

The data obtained indicate that the rate of curing non-modified ML-0136 varnish is much lower than that of samples modified with OAIF, the relative hardness of the coating varying as follows: ML-0136 < ML-0136 + 0.1% of OAIF < ML-0136 + + 0.5% of OAIF < ML-0136 + 1% of OAIF.

Physical-mechanical properties of varnish coatings

Parameter	Composition of the film-forming system, wt %					Non-modified ML-0136 varnish
	99.9 / 0.1	99.7 / 0.3	99.3 / 0.5	99.3 / 0.7	99.0 / 1.0	
Thickness of coating, microns	30	30	31	29	30	30
Resistance on exposure to flowing water at 20°C without visible changes, h	605.0	630.0	680.0	697.0	850.0	240.0
Pendulum hardness, rel. units	0.60	0.64	0.65	0.7	0.72	0.31
Impact strength of the coating film, kgf · cm	55	55	55	60	65	40
Flexural resilience, mm	1	1	1	1	1	1
Adhesion of film to the metal substrate, points	0	0	0	0	0	1

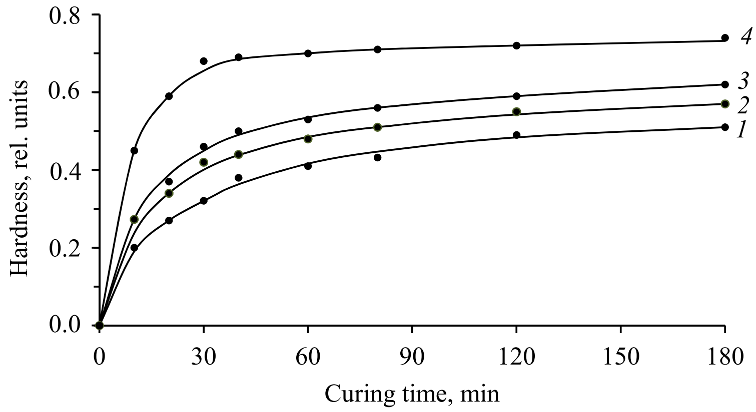


Fig. 2. Kinetics of ML-0136 varnish curing:
1 – without modifier; *2* – OAIF (0.1 wt %);
3 – OAIF (0.5 wt %); *4* – OAIF (1 wt %)

Conclusion. Thus, coatings based on the compound developed if compared with the unmodified ML-0136 resin possess higher hardness, strength, and adhesion while maintaining flexibility in bending, which ensures their resistance to abrasion and scratching. Water resistance of the modified compounds increases from 240.0 to 850.0 h without any visible change of the coating. The obtained results indicate that the reactive multifunctional modifier of OAIF melamine-alkyd resin is involved in the reactions of coating curing, contributing to the increase in the density of the polymer grid and the degree of coating curing.

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