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Modification of Alkyd and Alkyd-Melamine Binders with Imide-Containing Oligomers

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Abstract—This paper considers the possibility of modifying alkyd and alkyd-melamine binders with synthesized reactive imide-containing oligomeric modifiers. Using scanning electron microscopy, it is found that the addition of oligomeric imide-containing modifiers increases the protective effect of the anticorrosion coating made of modified resin almost threefold. It is shown that coatings formed from modified binders retain high levels of adhesion and impact strength and have increased hardness compared to coatings based on a binder without a modifier.

Keywords: alkyd oligomer, alkyd-melamine oligomer, oligomeric modifier, oligoimide, oligomer compatibility, protective properties

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Alkyd and alkyd-melamine resins are widely used as components in creating protective coatings for various purposes. However, these resins have certain disadvantages, for example, high brittleness, low hardness, and insufficient resistance to moisture, acids, and alkalis.

One way to improve the properties of these materials is to use monomers of various chemical structures in their synthesis. However, a more effective and affordable way to achieve the best compliance of the properties of coatings with the requirements of specific applications is, apparently, the introduction of small amounts of modifying agents into the composition of industrially produced polymer film-formers. The effectiveness of this approach is shown, for example, in [1, 2].

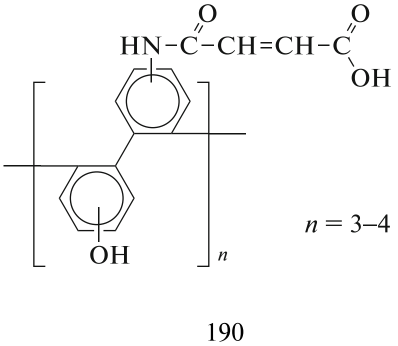
The aim of this work is to investigate the effect of reactive imide-containing oligomeric modifiers on the physicomechanical and protective properties of coatings (hardness, adhesion, impact strength, resistance to static effects of water, etc.) formed on the basis of alkyd and alkyd-melamine varnishes.

EXPERIMENTAL

The study was carried out using the industrially produced alkyd-melamine varnish ML-0136 (*TU 6-10-1392–78*), which is a solution of glycerol polyester of phthalic acid, modified with castor oil and supplemented with highly butanolized melamine-formaldehyde resin (MFR) K421-02, and alkyd resin synthesized using 5,6-benzobicyclo-[2,2,2]octanone-8-dicarboxylic-2,3 acid anhydride (ABBA) as an acid component.

As modifying agents for alkyd-melamine and alkyd resins, we used the following imide-containing oligomers:

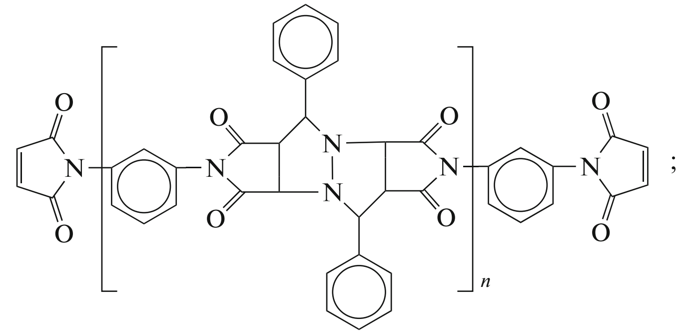
- oligohydroxymaleamido acid (OHFMAA),



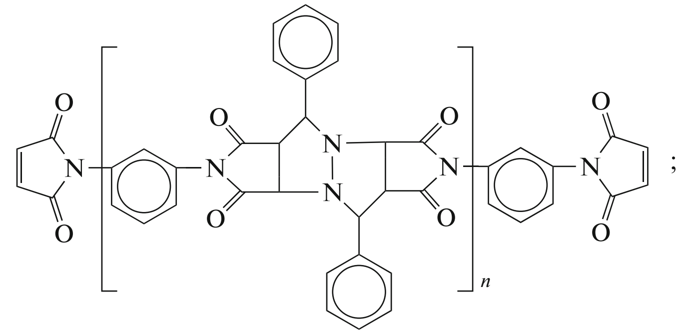
;

$n = 3–4$

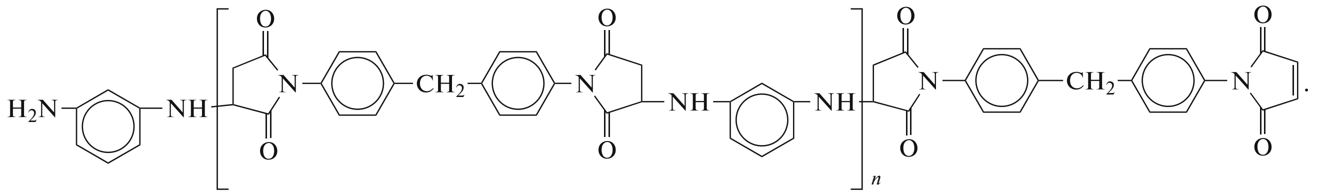
- oligomaleimidohydroxyphenylene (OMIHP),



- oligoimide based on benzalazine and *m*-phenylene-*bis*-maleinimide (OI),



- polymaleimidamine (PMIA),



Alkyd-melamine varnish was modified with all synthesized oligomers: OHFMAA, OMIHP, OI, and PMIA. Alkyd resin was used to prepare compositions only with OMIHP.

The choice of these film-formers as the main components of the compositions was determined by the presence of reactive groups in their molecular structure, which, under certain conditions, can interact with functional groups of imide-containing oligomers.

The choice of imide-containing oligomeric modifiers was determined by the presence of reactive maleimide end and side groups in their structure and the bulky structure of macromolecules. All synthesized compounds are readily soluble in polar aprotic solvents; in addition, OMIHP, PMIA, and OI have high thermal stability, which is due to imide cycles in the system: the temperature of 5% weight loss is 320°C for PMIA, 350°C for OMIHP, and 415°C for OI.

For preliminary assessment of the compatibility of polymers with each other and with oligomeric modifiers, Hildebrand solubility parameter δ was used. In this work, the compatibility was predicted by calculating parameter δ for various combinations of the oligomeric modifiers (OHFMAA, OMIHP, PMIA, and OI) and the main film-forming agents (MFR and alkyd resin).

Parameter δ was calculated according to [3], its SI base unit is $(J/m^3)^{1/2}$. The squared solubility parameter represents the cohesion energy density. The calculation was carried out using tabulated values of cohesion energy and van der Waals volumes of each type of atoms. For polymeric compounds, δ was estimated per repeating unit of the macromolecule. To assess the compatibility of film formers and modifiers, their solubility parameters are compared. When a difference in these values is small, the polymer mixture should form a stable solution: the closer the calculated values of parameter δ for the components of the compositions, the higher their compatibility with each other.

The calculated values of the Hildebrand solubility parameter for the modifying oligomers and alkyd and melamine-formaldehyde resins have only small differences, which suggests that there is thermodynamic compatibility of melamine-formaldehyde and alkyd

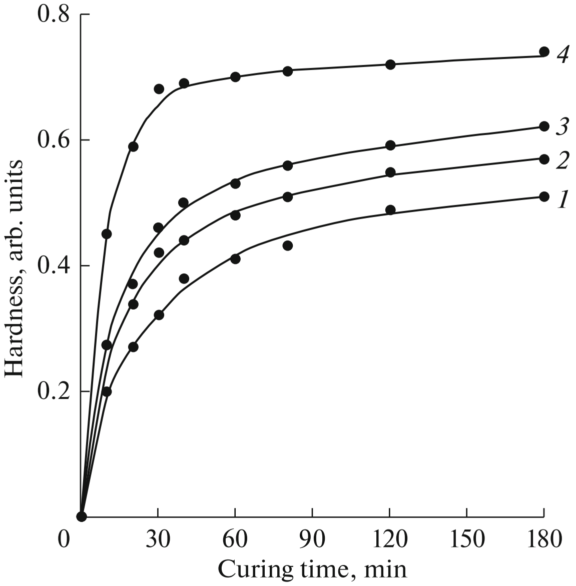


Fig. 1. Curing kinetics of varnish ML-0136 modified with imide-containing oligomers: (*1*) without modifier, (*2*) 3 wt % PMIA, (*3*) 3 wt % OI, and (*4*) 1 wt % OMIHP.

resins with all oligomers and allows using the latter as modifying additives:

Test substance	δ, $(J/m^3)^{1/2}$
Alkyd oligomer	19.8
MFR	24.0–26.0
OHFMAA	21.1
OMIHP	20.7
OI	20.5
PMIA	20.6

For alkyd with medium fat content, the total solubility parameter is 19.8 $(J/m^3)^{1/2}$. The composition of alkyd-melamine varnishes includes melamine-formaldehyde resin K-421–02, the total solubility parameter of which ranges within 24–26 $(J/m^3)^{1/2}$ [4].

It has been experimentally established that alkyd and alkyd-melamine resins combine well with solutions of the above oligomeric compounds, do not delaminate during prolonged storage, and produce well-formed coatings.

Film-forming compositions were obtained by introducing the calculated amounts of modifiers as 10% solutions in DMF into alkyd and alkyd-melamine varnishes and mixing the compositions until complete homogenization was achieved. The obtained compositions were used to prepare coating samples 25–35 μm thick in two different ways:

- by applying a layer of modified alkyd or alkyd-melamine varnish by casting directly onto metal substrates; and
- by forming a sublayer of OMIHP on a metal substrate, followed by removal of the solvent, drying in air at 25–30°C for 20–30 min, and applying a layer of alkyd or alkyd-melamine varnish modified with OMIHP.

Coatings based on alkyd-melamine varnish modified with OHFMAA, OI, and PMIA were formed only by the first method.

The main properties of imide-containing alkyd-melamine varnish coatings modified by OHFMAA, OMIHP, OI, and PMIA are presented in Table 1. It can be seen that the modified varnish, cured upon heating with the formation of three-dimensional products, forms coatings with high hardness and good adhesion, which provide enhanced corrosion resistance of metal surfaces against moisture due to components of the barrier and adhesive mechanism of the protective action of the coating in the presence of modifiers, each elementary unit of which contains adhesion-capable double bonds and hydroxyl and carboxyl groups.

It was found that the hardness of most samples of coatings made of varnish ML-0136 modified with the synthesized oligomers increases by about twofold in comparison with the coating of nonmodified varnish. The impact strength also increases by about 1.5-fold. The introduction of imide-containing modifiers at a certain concentration resulted in the highest adhesion score determined by the cross-cut method (*GOST* (State Standard) *15140–78*). The method for determining the bending elasticity of coatings (*GOST* (State Standard) *6806–73*) did not reveal any differences between the modified and nonmodified samples: all samples of varnish coatings were characterized by high elasticity; the coatings did not crack and did not peel off from the substrates when they were bent over a rod 1 mm in diameter.

Figure 1 shows experimental data regarding the kinetics of curing of the coatings formed from nonmodified varnish and from the compositions by measuring their relative hardness during curing at 130°C.

As can be seen from Fig. 1, hardness of the coatings for the modified samples with the same curing time is significantly higher compared to the nonmodified sample. The data obtained indicate that the curing rate of the nonmodified ML-0136 varnish is significantly lower than that of the samples modified with all the proposed oligomers. The relative hardness of the coating increases in the following order: ML-0136 < ML-0136 + PMIA < ML-0136 + OI < ML-0136 + OMIHP.

Figure 2 shows IR spectra of samples from nonmodified alkyd-melamine varnish and the varnish modified with 5 wt % OI, which were noncured and cured at 130°C for 30 min. The spectra indicate the participation of double maleimide bonds of oligomers in the curing of the compositions. The spectra of alkyd-melamine resin modified with OI show absorp-

Table 1. Main properties of alkyd-melamine coatings, nonmodified and modified with oligomeric imide-containing modifiers, cured at 130°C for 30 min

Composition	Film hardness, arb. units	Impact strength, cm	Adhesion to steel, points	Elasticity, mm	Resistance to static water exposure at 20°C, days
Nonmodified varnish ML-0136	0.31	40	1	1	7
ML-0136 + 0.1% OHFMAA	0.65	60	0	1	19
ML-0136 + 0.3% OHFMAA	0.67	60	0	1	22
ML-0136 + 0.5% OHFMAA	0.69	65	0	1	23
ML-0136 + 0.7% OHFMAA	0.71	65	0	1	25
ML-0136 + 1.0% OHFMAA	0.72	70	0	1	32
ML-0136 + 0.1% OMIHP	0.59	50	0	1	13
ML-0136 + 0.3% OMIHP	0.62	50	0	1	15
ML-0136 + 0.5% OMIHP	0.65	55	0	1	17
ML-0136 + 0.7% OMIHP	0.67	55	0	1	20
ML-0136 + 1.0% OMIHP	0.68	60	0	1	23
ML-0136 + 0.5% OI	0.38	60	1	1	—
ML-0136 + 1.0% OI	0.40	65	0	1	—
ML-0136 + 2.0% OI	0.45	70	0	1	—
ML-0136 + 3.0% OI	0.48	70	0	1	—
ML-0136 + 5.0% OI	0.52	85	0	1	—
ML-0136 + 0.5% PMIA	0.38	50	1	1	—
ML-0136 + 1.0% PMIA	0.40	55	1	1	—
ML-0136 + 2.0% PMIA	0.45	60	1	1	—
ML-0136 + 3.0% PMIA	0.48	60	0	1	10
ML-0136 + 5.0% PMIA	0.50	65	0	1	—

tion bands in the regions of 1080, 1030, and 1495 cm^{-1}, in-plane bending and stretching vibrations of the monosubstituted aromatic ring; 1186 cm^{-1}, bending vibrations of the C–N bond; 1380 cm^{-1}, vibrations of the C–N bond in five-membered imide rings; and 1605 cm^{-1}, stretching vibrations of the N–N bond. These peaks in the spectrum are due to the bonds in OI, as well as those formed during the curing of alkyd-melamine resin with the participation of OI. It is important that the peak in the frequency range of 1660 cm^{-1}, which is characteristic of nonconjugated double bonds, is absent in the cured composition, which indicates their complete consumption during the curing of the proposed composition.

Thus, the above results show that the introduction of modifying imide-containing oligomers into alkyd-melamine resin makes it possible to significantly increase the hardness of the modified coatings, which is due to the fact that the unsaturated bond in the maleimide end groups of modifiers, being electron-deficient, can easily open at elevated temperatures due to the proximity to carbonyl groups, interacting with >NH and $-NH_2$ groups of MFR to form a spatial polymer structure [5, 6].

This hypothesis is indirectly confirmed by the fact that the hardness of the coatings modified with OMIHP, which have reactive double bonds in each elementary unit, in contrast to other oligomers in which these fragments are contained only in the end groups, is higher than that of the coatings modified with OI and PMIA.

To determine the effect of OMIHP used as a modifier of alkyd-melamine varnish on the structure of the coating, we used electron microscopy to examine the surface of modified and nonmodified alkyd-melamine varnish coatings (Fig. 3).

To obtain information on the effect of the sublayer formed from OMIHP on a metal plate on the coating structure and to confirm its inhibitory effect on the corrosion process, photographs of the coatings formed directly on the metal plate and on the oligomeric sublayer from the side of the metal substrate were taken after holding the samples in aqueous medium at 20°C for 20 days.

Electron microscopic images show that the surface of the OMIHP-modified film (Fig. 3c) removed from the outside is flatter and smoother in than that of coatings made of nonmodified alkyd-melamine varnish

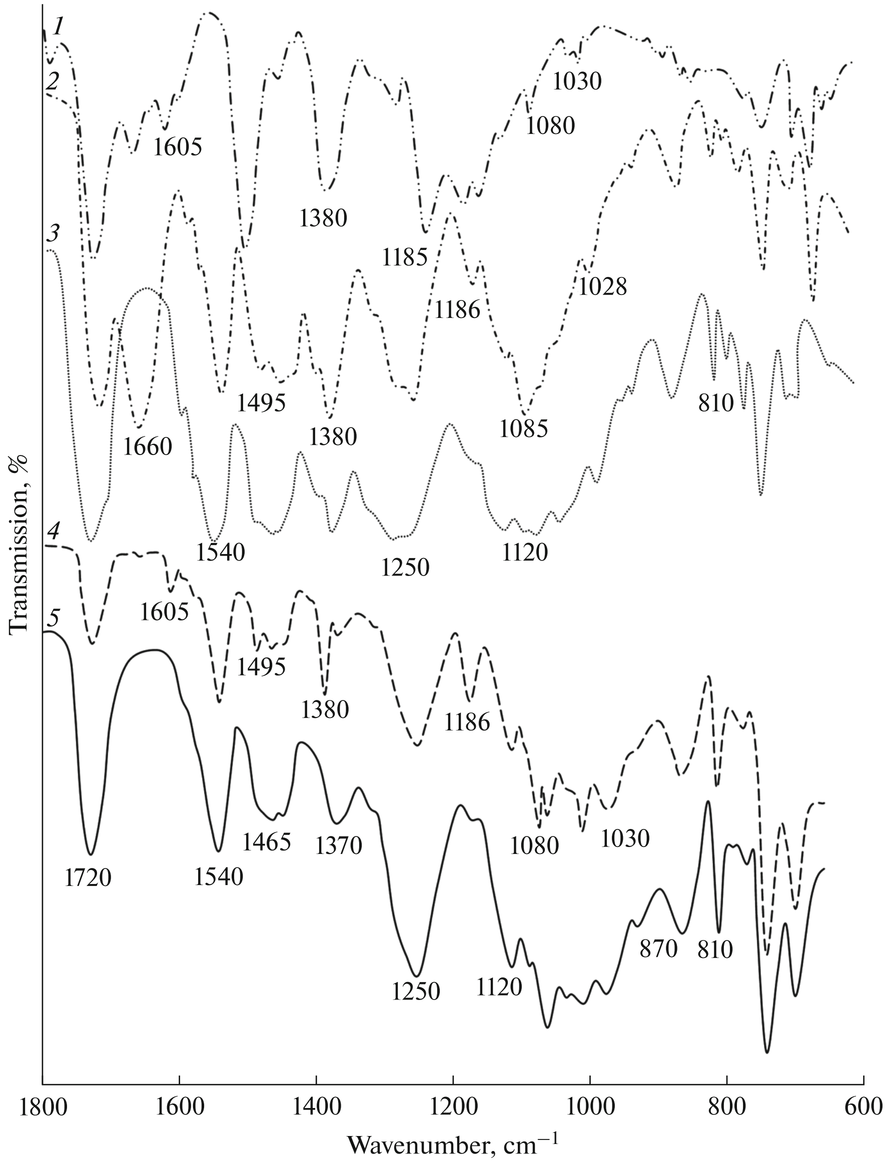


Fig. 2. IR spectra of alkyd-melamine resin ML-0136 modified with OI: (*1*) OI, (*2*) noncured resin modified with 5 wt % OI, (*3*) noncured nonmodified resin, (*4*) cured resin modified with 5 wt % OI, and (*5*) cured nonmodified resin.

(Fig. 3a). The micrographs of the inner surface of the films clearly show inorganic crystals grown into the coating surface. These are, most likely, corrosion products: iron oxides and iron hydroxides. It can be seen that the surface of the alkyd-melamine film, which was obtained by applying the modified composition to the oligomeric sublayer, is filled with crystals unevenly: there are areas of clear coating (Fig. 3d). The crystal size reaches 6–9 μm. In the case of applying a nonmodified alkyd-melamine coating directly to the metal plate, crystals have a different shape and densely cover the film surface (Fig. 3b). This method of forming the coating increases the average crystal size to up to 15–20 μm at the same time of exposure of the samples to aqueous medium. This, apparently, can be explained by the fact that metal ions, which migrate from the substrate into the polymer layer, are the growth centers for underfilm corrosion. The use of an imido-containing oligomer, the structure of which includes imide fragments, functional groups, and double bonds in maleimide rings, which improve the adhesive characteristics of the coating, slows down the formation of underfilm corrosion on steel substrates.

Since OMIHP is an effective modifier of alkyd-melamine resin, it was of interest to study its effect on the properties of compositions based on alkyd resin synthesized using ABBA as an acid component, as well as Gl and PEr as alcohol components. ABBA and ABBA-based alkyd resin were synthesized by existing methods.

It is known that the use of ABBA for the synthesis of alkyd resins makes it possible to improve the resistance of protective varnish coatings to UV radiation and increase their hardness and adhesion to substrates. The improvement in the operational properties of coatings is explained by the presence of condensed nuclei and a carbonyl group in the cycle in the ABBA molecule. To increase the atmospheric and water resistance of the coatings, in this work we modified alkyd resin with an imide-containing compound, OMIHP.

The amount of OMIHP introduced into alkyd resin was 0.5 wt %. Varnish compositions were cured to a dryness degree of 3 at 100°C over 30 min.

Table 2 presents data on the composition and properties of protective coatings obtained using alkyd resin modified by OMIHP. These data show that the hardness of the protective coatings, depending on the type of alcohol component, fat content of alkyd resin, and the modifier, varies from 0.65 to 0.98 arb. units. Introduction of the modifier slightly increases the hardness of the coatings; however, the formation of a primer layer from OMIHP does not affect the hardness of the coatings.

Apparently, this result can be explained by the fact that there is no chemical interaction between the resin and the modifier during the formation of a network structure. Coatings based on all the investigated compositions, regardless of the method of their application, are characterized by the maximal adhesion score (zero points on a six-point scale).

The introduction of OMIHP into alkyd resin has a significant effect on the ability of a film coating to protect metal surfaces from corrosion. Underfilm corrosion of metal coated with nonmodified alkyd resin begins after 65 days when the samples are exposed to water. The introduction of 0.5 wt % OMIHP into alkyd resin during the coating formation on a metal surface without a sublayer increases the protective effect by about 1.5-fold. This effect increases even more (almost threefold) when a protective coating of modified alkyd resin is applied to the OMIHP sublayer. This effect can be explained by the inhibitory effect of this modifier, which is consistent with the results of electron microscopy examination of alkyd-melamine coatings (see Fig. 3).

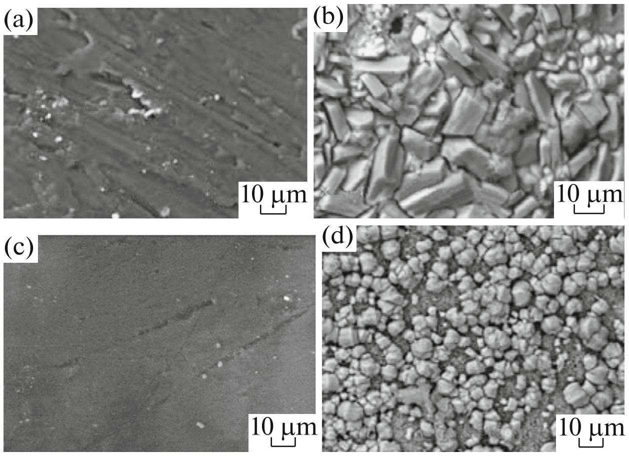


Fig. 3. Electron microscopy images of the (a, c) outer and (b, d) inner sides of the alkyd-melamine coating: (a, b) coating from nonmodified varnish ML-0136; (c, d) coating from ML-0136 varnish modified with 1 wt % OMIHP applied to an oligomeric sublayer. Magnification 1000×.

CONCLUSIONS

Thus, the introduction of 0.5–5 wt % of imide-containing reactive oligomers of various chemical structures into alkyd-melamine varnish makes it possible to vary the properties of coatings by quantitatively and qualitatively changing the compositions due to the formation of an additional network structure, increasing the hardness of the coatings twofold and the impact strength from 40 to 60–85 cm while maintaining their good adhesion to substrates and elasticity.

It was found that the efficiency of modifying alkyd-melamine resins with oligoimide additives, as well as the extent of improvement of their operational properties, increases upon transition from oligoimides, which contain only terminal maleimide groups, to oli-

Table 2. Composition and properties of varnish coatings based on alkyd resin

Resin composition			Coating hardness, arb. units			Resistance to static impact of water, days		
acidic component	alcohol component	fat content, %	alkyd resin	modified alkyd resin		alkyd resin	modified alkyd resin	
				without sublayer	with sublayer		without sublayer	with sublayer
ABBA	Gl	30	0.94	0.98	0.98	65	95	180
ABBA	Gl	40	0.92	0.94	0.94	66	97	180
ABBA	Gl	50	0.61	0.65	0.65	60	93	178
ABBA	PEr	50	0.83	0.86	0.86	45	80	155
ABBA	PEr	60	0.81	0.84	0.84	42	75	150

goimides with maleimide groups in the oligomeric chain.

The introduction of 0.5 wt % OMIHP into the composition of alkyd resin synthesized using 5,6-benzobicyclo-[2,2,2]-octanone-8-dicarboxylic-2,3 acid anhydride makes it possible to obtain coatings with hardness up to 0.65–0.98 arb. units and increase their water resistance 1.5-fold.

It was established that the introduction of OMIHP into alkyd-melamine resin and the formation of an oligomeric primer sublayer of OMIHP on the substrate has a positive effect on the coating structure, inhibits the process of underfilm corrosion of the substrate, and increases the protective effect of the anticorrosive coating made of modified alkyd resin almost threefold.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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