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INFLUENCE OF NANODIMENSIONAL ADDITIVES INJECTION METHOD ON THE PROPERTIES OF COATINGS ON THE BASE OF MODIFIED ALKYD AND EPOXY PRIMERS

For the first time influence of the carbon nanotubes obtained by catalyst synthesis in pseudoliquid layer and activated and non-activated carbon nanotubes obtained in high-tension discharge plasma on the mechanical-and-physical and protective properties of coating on the base of modified alkyd and epoxy primers was investigated.

Carbon nanotubes injection methods in the form of suspension in polar (acetone, cyclohexanone, butanol-1, ethyl cellosolve) and non-polar (*o*-dimethylbenzene) solvents for alkyd primers and in the form of suspension in P-5A solvent and curing agent for epoxy primer were examined.

In all cases the carbon nanotubes suspension in curing agent and solvent was produced by previous dispersion in cell ultrasonic bath during 15 minutes with further mixture during 20 minutes on laboratory dissolver with milling mixer.

The investigation showed that modification of the alkyd primer Belakor with carbon nanotubes suspension in polar solvents increases primer properties to a greater degree than carbon nanotubes suspension in non-polar solvents. For epoxy primers it was determined that modification with carbon nanotubes suspension in solvents is more effective than in curing agent. The modification of epoxy primer with carbon nanotubes suspension in curing agent decreases coating properties in many cases, probably because of functional groups adsorption on the surface of carbon nanotubes, which results in under-cured coatings; it can be seen from decreasing hardness, and consequently, protection properties.

Key words: primer, nanotubes, solvent, coating, hardness, salt resistance.

Introduction. Paint-and-varnish materials are multicomponent heterogeneous systems, so, the addition of even small amounts of carbon nanotubes (CNT) with large specific surface significantly changes the conformation of macromolecules of the film-forming agent due to the nanoparticles adsorbed on the surface and increases the degree of the coatings filling. CNT can also fill the voids between the particles of pigments and fillers. This affects the degree of paint-and-varnish coatings curing, which is evident from the change of their physical-mechanical and protective characteristics [1].

Main part. We investigated the effect of carbon nanotubes obtained by catalytic synthesis in a fluidized layer (CNT1), activated and non-activated carbon nanotubes (CNT2) formed in high-voltage discharge plasma, and the method of their introduction on the drying time, physical-mechanical (hardness, adhesion, impact strength) and protective (resistance to static action of water and sodium chloride solutions) properties of paint-and-varnish coatings.

The properties of unmodified and modified alkyd and epoxy primers of various brands and manufacturers: Ecol ГФ-021 (MAV), Metalgrund (Alpina), Belakor (MAV) EP-045 (JSC “Lakokraska”, Lida) produced in the Republic of Belarus, and Urekor S (Sniezka, Poland) were also studied.

During the investigation concerned the technique of adding carbon nanotubes to the pigmented coating materials, which consists in the preliminary dispersing them in the solvent or curing agent in the cell of Bandeline Sonorex ultrasonic bath (operating frequency of 40 kHz) for 15 min, followed by mixing for 20 min in the DISPERMAT®CA laboratory dissolver, using a milling rabble at the speed of 2000 rpm [2] was developed.

CNT were added to primers in the amounts of 0.005, 0.010 and 0.100% from the mass of paint-and-varnish material and dry residue, in the form of suspension in the solvent or curing agent.

Modified paint-and-varnish compounds were applied by pneumatic spraying onto standard substrates, i.e. special glass plates, their size being 90×120 mm and thickness of 1.2 mm (GOST 683); plates of 08 KP or 08 PS (GOST 16523) steels of 70×150 mm in size and 0.8–1.0 mm in thickness. Coatings were formed under natural conditions at the temperature of (20 ± 2)°C. Two days after the application, physical-mechanical properties of the coatings (hardness by pendulum device of TML type (the pendulum A (GOST 5233), impact strength (GOST 4765), cross-cut adhesion on the 4-point scale (GOST 15140), and after 10 days, the resistance to static action of aggressive media at the temperature of (20 ± 2)°C (GOST 9.403) were determined.

Effect of CNT on the properties of coatings based on alkyd primers. Table 1 presents the results of the study of alkyd primers characteristics and physical-mechanical and protective properties of paint-and-varnish coatings with them as a base.

Table 1

Properties of alkyd primers and coatings based on them

Index	Primer brand			
	Ecol GPH-021	Metalgrund	Belakor	Urekor S
Coating color	Brown	White	Gray	White
The degree of grinding, microns, no more than	40	30	30	30
Funnel viscosity by VZ-4 at the temperature of (20 ± 0,5)°C, no less than	147	160	91	129
Dried film covering ability, g/m^2, no more than	56.7	59.7	66.1	76.9
Percentages by mass of nonvolatile substances, no less than	61.7	73.6	53.0	67.0
Hardness by TML (A) pendulum, rel. units, no less than	0.32	0.26	0.38	0.13
Adhesion by cross-cut test method, points, no more than	1	3	1	3
Adhesion by cross-cut test method with back impact, cm, no less than	5	5	10	5
Impact strength, cm, no less than	100	10	60	50
Resistance to static action, days, no less than:				
– of water	1	8	4	2
– of 0.5% solution of NaCl	1	4	4	2
– of 3% solution of NaCl	1	4	4	2

Belakor primer is characterized with the best combination of physical-mechanical and protective properties. For this reason, the influence of CNT and the technique of their addition were further studied by using this paint-and-varnish material (Table 2).

Addition of CNT1 suspension in xylene in the amount of 0.01 and 0.10% to Belakor primer has led to an increase in the impact strength of the coatings by up to 90 and 100 cm, respectively, compared with unmodified – 60 cm, the modified coatings having lower protective attributes.

Modification of Belakor primer with activated and non-activated CNT2 (0.01%), pre-dispersed in xylene, did not result in significant changes in the physical-mechanical and protective properties of the coatings.

The researches involved permit to conclude that modification of CNT of different nature in the form of suspensions in non-polar solvents causes some minor improvement of physical-mechanical and protective properties of the primer coatings.

We also investigated the effect of nanotubes, while pre-dispersing them in polar solvents, such as acetone, hexanon, 1-butanol, ethyl cellosolve (Table 3) on Belakor primer which has the best combination of physical-mechanical properties. The solvents involved were selected from the most common ones in the paint-and-varnish industry with regard to their compatibility with alkyd film-forming agents (solubility parameters of the solvents are to be close to the parameter of solubility of the alkyd oligomer) [3].

Studies have shown that modifying Belakor primer of CNT 1 (0.01%) dispersed in polar solvents (acetone, hexanon, 1-butanol, ethyl cellosolve) in all cases resulted in the increase of coatings hardness by 3–7% for acetone and butanol-1 and 35% for cyclohexanone. Adding CNT 1 suspension to all the investigated polar solvents made it possible to improve the adhesion of the primer paint-and-varnish coatings by the cross-cut test method with back impact 1.5 to 4.0 times.

Table 2

Properties of coatings based on Belakor primer modified with CNT1 suspension in *o*-xylene

Index	Amount of CNT1, %			
	–	0.005	0.010	0.100
Hardness by TML (A) pendulum, rel. units, no less than	0.38	0.39	0.31	0.36
Adhesion by cross-cut test method, points, no more than	1	1	1	1
Adhesion by cross-cut test method with back impact, cm, no less than	10	10	10	40
Impact strength, cm, no less than	60	60	90	100
Resistance to static action, days, no less than:				
– of water	4	1	1	1
– of 0.5% solution of NaCl	4	1	1	1
– of 3% solution of NaCl	4	1	1	1

Table 3

Influence of solvent polarity and CNT1 on the properties of Belakor primer coatings

Index	Solvent / CNT1 concentration, %									
	o-xylene		acetone		cyclo-hexanone		butanol		ethyl cellosolve	
	0	0.01	0	0.01	0	0.01	0	0.01	0	0.01
Time of drying to degree 3 at temperature (20 ± 2)°C, min, no more	60	60	20	30	55	60	30	41	40	30
Hardness by TML (A) pendulum, rel. units, no less	0.38	0.31	0.40	0.41	0.35	0.47	0.23	0.25	0.20	0.19
Adhesion by cross-cut test method, points, no more than	1	1	2	1	1	1	1	1	1	1
Adhesion by cross-cut test method with back impact, cm, no less than	10	10	20	90	40	60	5	5	20	30
Impact strength, cm, no less than	60	90	100	100	100	100	100	100	100	100
Resistance to static action, days, no less than:										
– of water	4	1	1	6	1	1	1	1	1	1
– of 0.5% solution of NaCl	4	1	1	17	1	1	1	1	1	1
– of 3% solution of NaCl	4	1	3	12	1	2	3	3	1	1

Water resistance was increased 6 times when adding CNT1 suspension in acetone and salt-resistance was increased 2–3 times when adding CNT1 suspension in cyclohexanone and butanol.

Modification of activated and non-activated CNT2 (0.01%) pre-dispersed in polar solvents, in some cases increased coatings hardness by 10–70%, but improvement in the protective properties was not observed.

Studies have shown that modification of Belakor alkyd primer with CNT1 suspensions in polar solvents brings about more significant improvement of primer coatings properties than when using suspensions in nonpolar solvents. However, it should be taken into consideration, that the presence of a polar solvent in the paint-and-varnish compound may lead to increased water absorption of the polymer film, as in the paint and varnish coating formed there is a slight amount of residual solvents. Significant improvement of the protective properties has been observed when modifying with CNT1 suspension in acetone. Perhaps, it is due to the fact that this solvent is more volatile, which reduces the probability of the presence of its residues in the coating formed.

Improvement of physical-mechanical properties of most coatings on the base of the carbon nanotubes modified suspensions in the polar solvent of Belakor primer is due to a change in the conformation of macromolecules directly in paint-and-varnish material, which results in higher degree of coatings curing. However, the presence of residual polar solvents (with the exception of the composition including acetone), despite the improvement of adhesion and hardness, has not allowed to increase the protective properties of the modified primer coatings.

Effect of CNT on the properties of coatings based on epoxy primer. EP-045 epoxy primer is two-pack composition of natural drying, consisting of semi-finished primer and E-45 curing agent, i.e. solution of polyamide resin in xylene. Coatings based on this film-former have higher protective properties than alkyd ones.

We also investigated the influence of CNT on the physical-mechanical and protective properties of coatings based on modified epoxy primer, the former being added in two ways:

1) in the form of suspension in P-5A solvent (Table 4);

2) in the form of suspension in curing agent (Table 5).

Effect of CNT suspensions in solvent on the properties of primer coatings. Table 4 presents the results of the study of physical-mechanical and protective properties of the primer coatings based on EP-045 epoxy primer modified with CNT suspension of different nature in P-5A solvent.

Water resistance of all the coatings based on EP-045 epoxy primer, both modified and unmodified with carbon nanotubes, is rather high and is more than 40 days.

Modifying by the first method with practically any concentration of CNT, especially for CNT1 and non-activated CNT2 (0.01, 0.10%) resulted in a significant increase in coatings salt resistance – 2–3 times. When modifying EP-045 primer with suspension of activated CNT2 (0.005 and 0.100%) in the solvent the hardness of coatings increased by 15–20%, the adhesion by cross-cut test method with return kick being also improved 6 times, while impact strength remaining at the same high level of 90 cm.

Table 4

Properties of coatings based on EP-045 primer modified with CNT suspension in solvent

Index	CNT amount, %									
	–	CNT1			CNT2 non-activated			CNT2 activated		
		0. 005	0.010	0.100	0.005	0.010	0.100	0.005	0.010	0.100
Hardness by TML (A) pendulum, rel. units, no less than	0.35	0.41	0.30	0.42	0.36	0.36	0.36	0.41	0.30	0.42
Adhesion by cross-cut test method, points, no more than	1	1	1	1	1	1	1	1	1	1
Adhesion by cross-cut test method with back impact, cm, no less than	5	5	5	5	5	5	5	30	30	30
Impact strength, cm, no less than	90	45	50	70	90	50	35	90	90	90
Resistance to static action, days, no less than:										
– of water	40	40	40	40	40	40	40	40	40	40
– of 0.5% solution of NaCl	7	12	20	20	8	18	14	7	7	8
– of 3% solution of NaCl	3	2	7	17	18	18	18	8	3	7

Table 5

Properties of coatings based on EP-045 primer modified with CNT suspension in curing agent

Index	CNT amount, %									
	–	CNT1			CNT2 non-activated			CNT2 activated		
		0.005	0.010	0.100	0.005	0.010	0.100	0.005	0.010	0.100
Hardness by TML (A) pendulum, rel. units, no less than	0.47	0.34	0.31	0.31	0.43	0.37	0.43	0.47	0.27	0.30
Adhesion by cross-cut test method, points, no more than	1	1	1	1	1	1	1	1	1	1
Impact strength, cm, no less than	90	90	90	90	80	80	80	90	80	90
Resistance to static action, days, no less than:										
– of water	40	40	40	40	40	40	40	40	40	40
– of 0.5% solution of NaCl	7	9	9	2	2	3	9	7	5	5
– of 3% solution of NaCl	3	4	3	6	3	3	3	3	3	7

Effect of CNT suspensions in E-045 curing agent on the properties of primer coatings. Modifying EP-045 epoxy primer by the second method in many cases led to the deterioration of the properties of paint-and-varnish coatings, thus, the hardness of the coatings decreased by 10–40%. This is probably due to adsorption of the curing agent functional groups on the CNT surface and leads to under-cured coatings, reducing their hardness, and, consequently, their protective properties.

Studies have shown that the modification of EP-045 epoxy primer is feasible only in the case of adding CNT1 and non-activated CNT2 in the amount of 0.01 and 0.10% (of the weight of the paint-and-varnish material, taking into account the dry residue) in the form of suspension in the solvent, which causes significant improvement in the primer coatings salt resistance.

Conclusion. The researches involved make it possible to conclude that the modifying properties of CNT are influenced not only by the method of their synthesis and concentration, but also by the method of their addition, the composition of suspensions, in particular, the polarity of the solvents used and the presence or absence of a curing agent.

Modification of the alkyd primer by CNT suspensions in polar solvents results in significantly improved physical-mechanical as well as protective properties of the primer coatings rather than by those in non-polar solvents. When selecting polar solvents it is necessary to consider their affinity to the alkyd oligomers and volatility in order to prevent the shortening of the paint-and-varnish compounds shelf-life and the increase of water absorption of coatings based on them.

When modifying two-can paint-and-varnish materials, epoxy ones in particular, it is necessary to add CNT in the form of suspension in the solvent, but not in the curing agent, since functional groups of the latter are adsorbed on the surface of CNT.

References

1. Shashok Zh. S., Prokopchuk N. R. *Primeneniye uglerodnykh nanomaterialov v polymernykh kompozitsiyakh* [The application of carbon nanomaterials in polymer compositions]. Minsk: BGTU Publ., 2014. 232 p.

2. Shutova A. L., Sabadakha E. N., Prokopchuk N. R., Khovanskaya E. I. Influence of injection method of nanoadditive on the properties of coating on the base of modified alkyd primer. *Tezisy 79-y nauch.-tekhn. konferentsii professorsko-prepodavatel'skogo sostava, nauchnykh sotrudnikov i aspirantov (Tekhnologiya organicheskikh veshchestv)* [Thesis of 79th Scientific and Technical Conference of Teaching Staff (The Technology of organic compounds)]. Minsk, 2015. pp. 62 (in Russian).

3. Drinberg S. A. *Rastvoriteli dlya lakokrasochnykh materialov* [Solvents in paint industry]. St. Petersburg, KHIMIZDAT Publ., 2003. 240 p.

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