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Speakers are invited to submit papers till
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WELCOME IN THE RUSSIAN COATINGS WORLD!

Last year Russian economics faced global challenges: fall of oil prices, depreciation of the national currency, economic sanctions from US and EU and Russian countersanctions. These and other factors have caused stagflation and Russian coatings industry experienced some difficulties too (p.4).



But, just as adage goes, every cloud has a silver lining, the cheap national currency makes national products more appealing, and sanctions prompt import substitution and development of domestic production. This means that Russian paints producers have a chance to occupy new niches, because in some areas — marine, OEM coatings, coil coating — imported paints have a 45–80% share. Of course, nobody is dreaming of replacing all imported goods. It's impossible and not necessary, but getting a bigger share is desirable for every company. In this digest we present selected technical articles that show the directions in which Russian specialists are working.

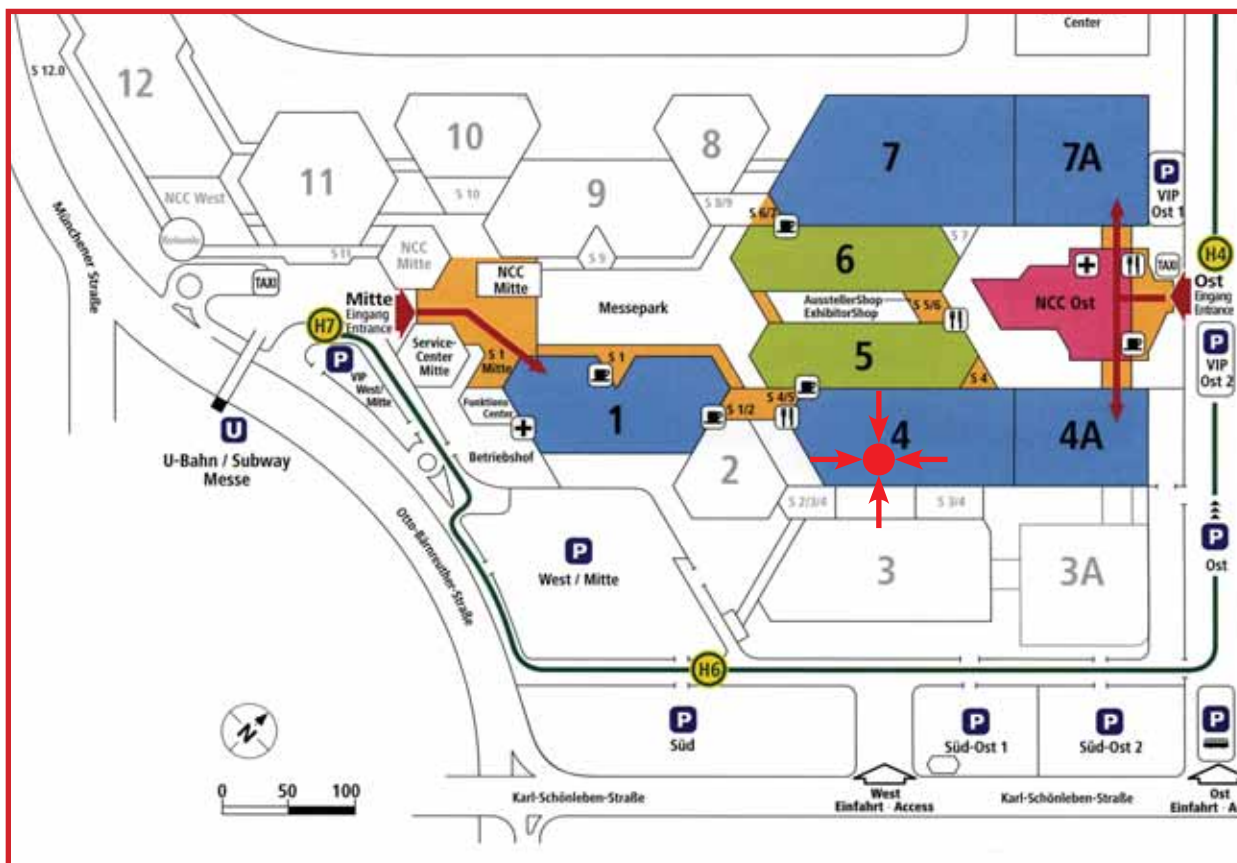
The weakest link in the grandiose plans for vast import replacement is the deficiency in domestic raw materials. Additives, binders with special properties, some kinds of pigments are not produced in Russia and will not be produced in the nearest future. That is why none of the European raw materials producers and suppliers has left the Russian market. But still, the high prices for European chemicals push formulators towards finding a replacement, and the current situation is a great chance for newcomers to the Russian market, that can compete with their prices and/or replacement technologies.

That's why I say: welcome in Russia! Our journal will help to popularize your products among customers in Russia and CIS.

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Best regards

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M.Yu. Kvasnikov, I.A. Krylova, I.F. Utkina, V.V. Tsvetkova, V.S. Tochilkina, A.S. Terekhov

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RUSSIAN COATINGS INDUSTRY IN 2014

O. Andrutskaya

Early last year, we reviewed optimistic and pessimistic scenarios for the industry in 2014; however, the turn of events involving the fall in oil prices, sanctions, fall of the national currency, which had affected the entire Russian economy, was totally unexpected.

The growth rate of the economy has slowed down, as evidenced by the gross domestic product (GDP) dynamics. According to the Federal State Statistics Service, in 2014, Russia's GDP grew by mere 0.6% year-to-year and, based on current prices, and constituted 70 trln 975,8 bn roubles, while in 2013 it grew by 1.3%.

Nevertheless, it should be admitted, that, in the environment of falling oil prices, geopolitical tensions, capital flight and Western sanctions, much worse performance might have been expected. Meanwhile, from February to October last year, industrial production displayed a positive trend with fluctuations in the 0–2.8% range. It was only in November that we saw a 0.4% drop in the output. On the whole, according to the Federal State Statistics Service data, in 2014, Russia's industrial production grew by 1.7% year-on-year, incl. 3.9% in December — the highest rate since April 2012. Seasonal and calendar factors omitted, industrial production in December 2014 increased by 2.1% from November, following a 1.1% decrease in November and 0.4% growth in October.

Generally speaking, December is one of the most favourable periods for the industry due to the completion of the annual production cycle associated with the finalised settlements with customers and suppliers, shipped products, payments and recovery of debts. Furthermore, businesses have not had time to experience in full the negative impact of rising key interest rates on loans.

PAINT AND COATINGS INDUSTRY

According to the Federal State Statistics Service, we see an overall decline in production in the previous year, which is not surprising, given the close relationship between the production of paints and the state of the industry, building and construction sector, and household income. Although some positive results were achieved in the water-based materials group, the overall performance was aggravated by the decline in the production of organic solvent-based paints (see Table 1). The dry oils group also contributed to the overall decrease, however, the demand for, and, therefore, the production of these products has been declining steadily over the last 20 years (in 1995, about 50 thousand tons were produced), thus, it is difficult to interpret the 2014 indicators with any reliability – whether the drop in this group is associated with the overall domestic economic situation or scheduled replacement of the obsolete product range is taking place.

By the end of the year, almost all companies had reduced their output (Table 2), which is natural for a seasonal drop in demand, however, some of them, for example, Meffert Invest LLC and Akzo Nobel Decor CJSC, manufactured more products in December compared to September (see Russian Coatings Journal, No. 11, 2014, p. 13). It might have been a temporary surge in demand driven by increased inflation expectations («buy before prices go up»), with distributors hurriedly stocking up.

As shown in Tables 3 and 4, production of water-based materials exceeds that of organic solvent thinnable ones, which might be on the whole welcome, but it is not that simple to explain why the 9 months' data shows a small, but noticeable margin in favour of organic solvent thinnable paint materials, with a reversal by the end of the season.

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Table 1. Coatings production in the Russian Federation, January to December, 2012-2014, tons

Group	January to December, 2012	January to December, 2013	January to December, 2014	2014/2013, %
Paints based on synthetic polymers or chemically modified polymers in an aqueous medium	392,847.2	423,814.4	433,304.2	102.2 (+2.2)
Paints based on synthetic polymers or chemically modified natural polymers in a non-aqueous medium	440,092.5	453,703.2	419,384.1	92.4 (-7.6)
Dry oils	18,127.3	19,552.6	18,678.1	95.5% (-4.5)
Total key groups	851,067	899,070	871,366.4	96.9 (-3.1)
Other	285,051	351,525	376,137.5	107 (+7.0)
Total, tons	1,136,118	1,248,595	1,247,504	99.9 (-0.1)

Table 2. Production of polymer-based paint materials, tons

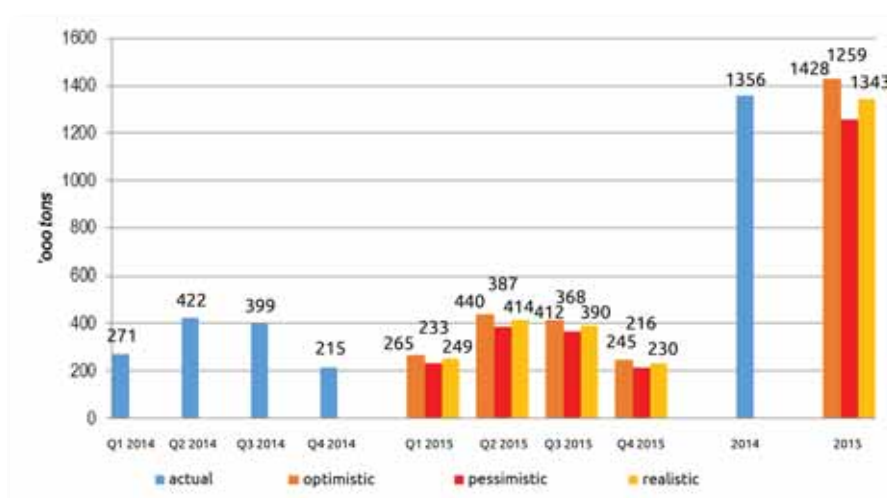
Company/output	December 2014	January to December, 2014
Total in the Russian Federation	46,586.8	853,155.1
Incl.:		
Tikkurila LLC	5,025	90,025
Lakra Sintez LLC	3,781	66,227
Predpriyatiye VGT LLC	1,976	46,101
Dekart CJSC	1,003	27,511
ABC Farben CJSC	724	26,541
Meffert Invest LLC	1,786	22,859.4
Khimik CJSC	890	21,795
Empils CJSC	0	21,638
Akzo Nobel Decor CJSC	1,976	18,299
Russkiye Kraski OJSC	912.3	18,199.3
Lakokrasochniye Materialy CJSC	919	16,589
«Saiver» Shelanger Chemical Factory OJSC	468	15,017
Stolyar LLC	809	12,444
LKM Group LLC	1,119	12,174.2
YPK YarLI CJSC	934.7	12,157.7
Yaroslavl Paint & Varnish Company LLC	1,213	11,190.9
Eskaro Chemical AS LLC	567	11,098
Yaroslavskiy Kraski	318.6	8,157.6
Total for 18 companies		458,024.1

Table 3. Production of water-based paints, tons

Company/output	December 2014	January to December, 2014
Total in the Russian Federation	26,051.6	433,304.2
Incl.:		
Tikkurila LLC	4,355	65,622
Predpriyatiye VGT LLC	1,976	46,101
Lakra Sintez LLC	2,866	37,251
Dekart CJSC	931	25,522
Meffert Invest LLC	1,786	22,859.4
Akzo Nobel Decor CJSC	1,976	18,299
Stolyar LLC	809	12,444
ABC Farben CJSC	400	9,903
Raduga Paint and Varnish Factory LLC	762	9,460
Alkyd LLC	0	8,541
Yaroslavskiy Kraski Association OJSC	293.1	7,220.7
Total for 11 companies		263,223.1

Table 4. Production of solvent based paints, tons

Company/output	December 2014	January to December, 2014
Total in the Russian Federation	20,440	419,384.1
Incl.:		
Lakra Sintez LLC	915	28,976
Tikkurila LLC	670	24,403
Khimik CJSC	709	19,022
Ruskiye Kraski OJSC	905.1	17,779
ABC Farben CJSC	324	16,638
Empils CJSC	0	15,094
Lakokrasochniye Materialy CJSC	798	14,180
LKM Group LLC	1,119	12,174.2
«Saiver» Shelanger Chemical Factory OJSC	289	11,967
YPK YarLI CJSC	911.5	11,856.2
Eskaro Chemical AS LLC	567	11,098
Yaroslavl Paint & Varnish Company LLC	1,149.6	10,656.2
Pigment OJSC	0	9,781
Petrocom – Lipetsk LLC	1,011	9,562
Kraski Kvil Factory LLC	533	9,308
Belcolor LLC	170	9,287
Total for 16 companies		202,805.6



What can we expect in the coming year? Naturally, no one is expecting any easy living: the Ministry of Economic Development of the Russian Federation forecasts a 3% shrinkage in Russia's GDP in 2015, while the European Bank for Reconstruction and Development (EBRD) predicts that Russia's GDP will drop by 4.8% this year. Experts from Russia's Higher School of Economics believe that «in the next two years Russia will face recession in the economy, starting not on January 1, 2015, exactly, but postponed until late February – early March, when the manufacturers' stocks will have been exhausted, and costs of purchasing new materials are much higher». Rising prices of raw materials have spanned all industries, becoming the highest in the last 16 years, while the key driver of this increase is the weakening

rouble that has lost 30% of its value against the dollar since early 2014. In our industry, the price of imported products in the national currency has increased for dispersions, inorganic and organic pigments, microcalcite, titanium dioxide, mineral spirit. This means that the paint and varnish manufacturers will have to raise prices for their products. The industrial sector will apparently achieve some acceptable profitability, while the decorative sector, particularly DIY, will obviously face difficulties.

According to Chem-Courier analysis agency, in 2015, the Russian coatings market will decrease by 7%; pessimistic, optimistic and realistic projections are presented in the diagram.

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APPLICATION OF EPOXY ESTER IN WATER DISPERSION PAINTS PRODUCTION

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Film formation from water dispersions of polymers is connected with the sol-gel transition and is followed by spontaneous compression of formed intermediate gel to the state of monolithic film, while molecules of surfactants contained on the surface of the globules are dissolved in a polymer, or are pushed out from interglobular space, forming an independent phase. One of the ways to increase the quality of the formed film is the introduction of waterborne oligomers into the composition, which after curing may build in the polymer matrix. Previously it was shown [1] that epoxy esters can be used as oligomeric surfactants, in particular, for the surface treatment of pigments. The effect of polydispersity [1], the content of carboxylic groups and unsaturation of the residue of tall oil fatty acids used in the oligomer synthesis on the rheological properties of solutions and the change in these properties when diluted was shown.

To assess feasibility of epoxy ester as a dispersant and the stabilizer of aqueous dispersions of pigments we studied adsorption of water-soluble epoxy ester with the acid number of 88.4 mg KOH/g on the surface of the yellow iron oxide, chromium oxide and blue phthalocyanine.

Fig. 1–3 shows the isothermic lines of oligomer adsorption on these pigments.

Adsorption isotherms for all the studied pigments show polymolecular character. And as to the yellow iron oxide pigment there is significant chemisorption, connected with formation of insoluble film from iron salts on the surface of the pigment particles. These results comply with the data on adsorption of stearic acid on this pigment given in [2, p. 36]. The cause of its chemisorption is similar to the cause of the chemisorption of epoxy ester.

Grinding of pigments in obtaining pigment intermediate was carried out in dissolver in the medium, which is a water solution of the thickener (hydroxyethyl cellulose), dispersant (sodium tripolyphosphate), antifreeze (ethylene glycol), defoamer (BYK-024) and different amounts of water-soluble epoxy ester. The effectiveness of dispersion in dissolver is determined by the hydrodynamic conditions, depending on the viscosity of the medium [3].

To estimate the influence of epoxy ester on the rheological properties of the medium for dispersion we received viscosity curves for its different content, shown on Fig. 4.

These data show that the medium for the intermediate reveals clearly defined dilatant properties. The introduction of the epoxy ester (less than 1.5 %) in its composition increases viscosity, but significantly reduces the dilatancy, which almost vanishes at shear rates exceeding 700 s^{-1} and nature of flow approaches to the newtonian one. Such character of the flow is preferable for grinding of pigments and fillers using dissolvers [3]. Increasing content of epoxy ester to 2% results in dilatancy.

On the example of three pigments of different nature: yellow iron oxide ($\alpha\text{-FeOOH}$), chromium oxide (Cr_2O_3) and blue phthalocyanine ($\alpha\text{-copper tetrabenzotetraazoporphin}$) were studied processes of stabilization of their dispersion in the medium of the intermediate. The process of sedimentation of pigments in the medium was studied by measuring the change of optical density of dispersions in time [4]. Fig. 5 shows the curves of changes of optical density of the pigment dis-



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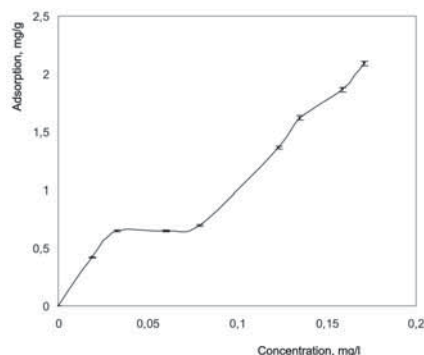


Fig. 1. Isotherm of the oligomer adsorption on the surface of phthalocyanine blue

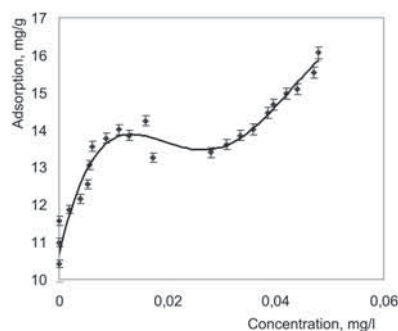


Fig. 2. Isotherm of the oligomer adsorption on the surface of yellow iron oxide

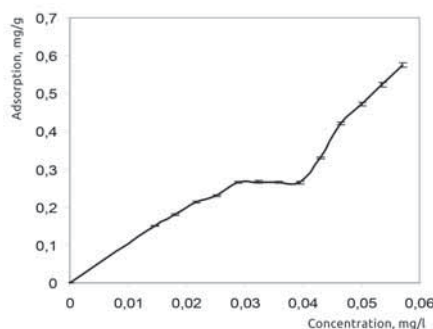


Fig. 3. Isotherm of the oligomer adsorption on the surface of chromium oxide

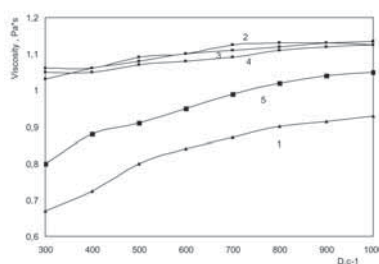


Fig. 4. Rheological properties of the medium for the water intermediates with different content of epoxy ester : 1 — without epoxy ester; 2— 0,5% ; 3 — 1%; 4 — 1,5%; 5 — 2% (D — shear rate)

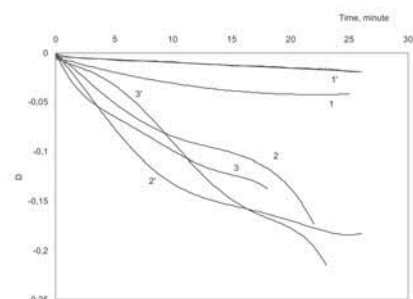


Fig. 5. Change in the optical density (D) of dispersions of pigments in the medium of the water intermediate. 1 — yellow iron oxide; 2 — blue phthalocyanine; 3 — chromium oxide; 1', 2' and 3' — with the additive of oligomer

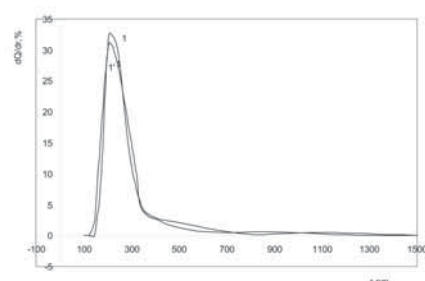


Fig. 6. Differential curves of the particles size distribution for the samples of yellow iron oxide pigment paste, selected after 2 minutes prior the dispersion in the water intermediate (1) with water-soluble epoxy ester added (1')

persions in water intermediate containing 1.5% of epoxy ester. Based on these data, the initial rate of sedimentation of pigments in these suspensions were calculated. The calculation results are given in Table 1.

These data show that the introduction of water-soluble epoxy ester in water intermediate, designed for dispersion of pigments to obtain water dispersion paints, results in decrease in the rate of sedimentation and accordingly to increase of their stability. So, for iron oxide pigment the sedimentation rate in the presence of epoxy ester decreases 1,2 times, oxide of chromium and copper phthalocyanine — almost 2 times.

The effectiveness of water-soluble epoxy ester as a dispersant has been evaluated according to the results of processability analysis and increase of optical effectiveness of pigments in the process of grinding. To that effect at stated intervals samples of pigment paste were selected,

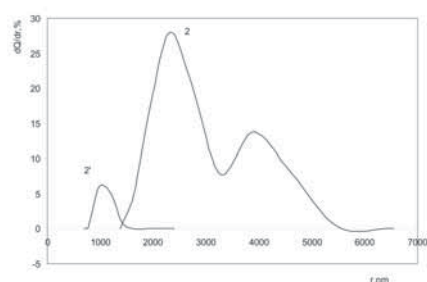


Fig. 7. Differential curves of the particles size distribution for the samples of blue phthalocyanine pigment paste, selected after 10 minutes from the start of the dispersion in the water intermediate (2) with water-soluble epoxy ester added (2')

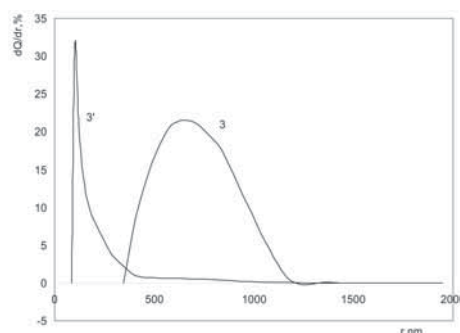


Fig. 8. Differential curves of the particles size distribution for the samples of chromium oxide paste selected after 5 minutes from the beginning of the dispersion in the water intermediate (3) with water-soluble epoxy ester added (3')

ide demonstrate significant shift of curves towards greater dispersion. The dispersion content of the iron oxide pigment remains virtually unchanged, but the stability of its dispersion increases significantly. And as shown below, the consumption of energy needed for its grinding is reduced. In this case the adsorption layer of the modifier, preventing secondary aggregation, accelerates an increase in the optical efficiency in dispersion.

The assessment of dispersion process by changing Kubelka-Munk function has shown considerable efficiency of the use of epoxy ester as a dispersant. So, the grinding resistance decreases in 30 times for iron oxide pigment, in 5 times for chromium oxide pigment and a half times for phthalocyanine pigment. That gives the chance to save energy for dispersion.

According to the results of analysis of dispersability and grinding parameters it can be concluded that the introduction of water soluble epoxy ester in water intermediate improves the efficiency of dispersion. Thus, it was demonstrated positive effects of epoxy ester additives on the dispersability of pigments and stability of their mixes with water (pastes).

Table 1. The Initial rates of deposition of pigment dispersions in the water intermediate in the presence of water-soluble epoxy ester

Pigment	Initial deposition rate, min ⁻¹	
	without oligomer	with the additive
Yellow iron oxide	-0,0036	-0,0030
Chromium oxide	-0,0044	-0,0024
Blue phthalocyanine	-0,0047	-0,0025

Table 2. Parameters of the grinding of pigments in the water intermediate (K_p — constant of grinding rate, F_∞ — limiting value of the Kubelka-Munk function, $t_{0,5}$ — grinding resistance)

Parameters	Pigments					
	Yellow iron oxide		Chromium oxide		Blue phthalocyanine	
	Without oligomer	+1,5% oligomer	Without oligomer	+1,5% oligomer	Without oligomer	+1,5% oligomer
K_D	6,9	156,2	2,6	12,3	2,2	3,5
F_∞	11,1	8,9	2,7	2,6	5,7	5,9
$t_{0,5}, \text{ min}$	1,5	0,05	1,0	0,2	2,6	1,7

their colouring ability and particle sizes distribution was determined by the method of low-angle scattering of laser radiation using Nanotract Ultra 151.

Figs. 6–8 show the results of dispersivity analysis in the samples of pigment pastes selected in the course of dispersion. Table 2 shows parameters of the process of dispersion, determined according to the optical efficiency of color pigments.

As shown on Figs. 6–8, the particles size distribution curves of copper phthalocyanine and chrome ox-

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STABILIZATION OF MODIFIED SILICONE EMULSION IN WATER BY ETHYLENE OXIDE NONIONIC SURFACTANTS

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INTRODUCTION

Silicone liquids and their emulsions are widely used as silicone anti-adhesive lubricant for press forms, oils, damping fluids, heat conductors and coolants, sealing compounds, defoamers, sealants. Sealants are used for sealing and bonding all types of joints and junctions where reliable isolation from environmental influences, good water resistance, durability and elasticity are needed. High-quality silicones are used in medicine as well.

Durability of buildings and constructions depends on many factors but one of the most important is the level of buildings' protection from aggressive influence of environment and, primarily, from humidity.

The most common way of waterproofing materials is to cover the surface with fats or waxes. For example, wood, tissue and paper preservation treatment with oils, paraffin waxes, ceresin, halowax and others. But deliberately high viscosity and poor penetration of oils and waxes into pinholes of hydrophilic substrates prevents uniform coverage of the surface. Besides such substances do not provide thermal and mechanical protection, durability, and compromise some properties of the protected material: reduce its vapor permeability, impair appearance, etc.

Other prospective way of hydroisolation is hydrophobization by application of special substances — water-repellent agents. It results in sharp reduction of objects' and materials' ability to be moistened by water and water solutions, preserving vapor and gas permeability.

Water-repellent agents based on organosilicone compound that create thin invisible permeable waterproof film are of great effectiveness. Such film is long term, chemically stable and resistant to low and high temperatures and possess good mechanical properties [1].

There are many wastes during production of items made from silicone rubber and secondary silicone (tubes, films, shims, cables) of different marks. Their utilization and processing is not an easy task. In connection with this, recycling such wastes is a topical issue.

The aim of this research is to obtain liquid oligomeric mixture of modified silicone by recycling silicone rubber wastes and items made from silicone with technology registered by LLC VESTO [2], and to get stable emulsion of modified silicone in water.

RESULTS OF RESEARCH AND DISCUSSION

The product received after recycling is called modified silicone MS-1. MS-1 is a viscous fluid of grey-white colour, well dispersed in hydrocarbon solvent. Density at 20 °C is 1.05–1.10 g/ml, viscosity at fluidity meter VZ-4 ≥ 20 s which is approximately 70 mPa. The product has alkaline reaction, pH=10–12, is not diluted in water. Main area of application is using MS-1 as water-repellent agent, hydrophobizing and plastifying additive to paints, bitumen and cements. Easily mixes with plaster and cement mortar. Adding hydrocarbon solvents or heating is needed to



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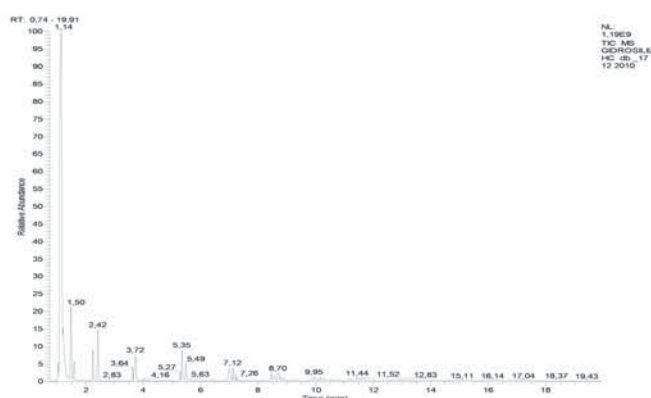


Fig. 1. Mass spectrogram MS-1 (general)

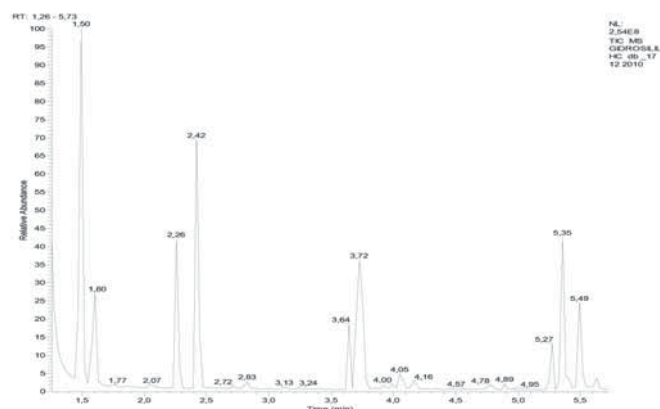


Fig. 2. Mass spectrogram MS-1 (area of main peaks)

Tab. 1. Results of gas chromatography-mass spectrometry of additives of the sample MS-1

Time of exit (min)	Name/elementary formula	Chemical structure	M	Abundance ratio, %
1,58	Tetraethoxysilane $C_8H_{20}O_4Si$		208	37,1
4,08	Trimethyltsiethoxycyclotri-siloxan $C_9H_{24}O_6Si_3$		312	28,26
7,28	Trimethylpentaethoxycyclotetra-siloxane $C_{13}H_{34}O_9Si_4$		446	16,82
10,08	Methylheptaethoxyhydra-cyclatetrasiloxane $C_{17}H_{44}O_{12}Si_5$		580	4,43
2,42	Dimethyltetraethoxydi-siloxane $C_{10}H_{26}O_5Si_2$		282	2,4
1,01	Ethanol C_2H_6O	CH_3-CH_2-OH	46	2,25
12,49	Decaethoxycyclopenta-siloxane $C_{20}H_{50}O_{14}Si_5$		654	2,05
5,49	Hexaethoxycyclotrisiloxane $C_{12}H_{30}O_9Si_3$		402	1,52
9,89	Heptaethoxypropoxydihydri-cyclopentasiloxane $C_{17}H_{44}O_{12}Si_5$		580	1,06

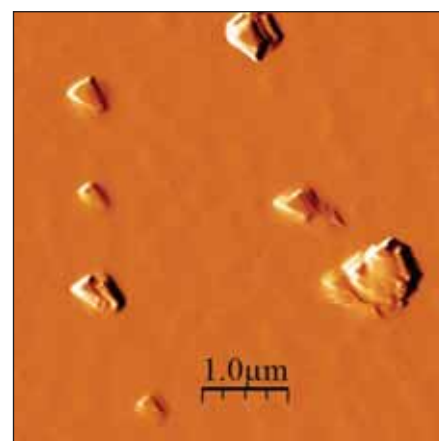
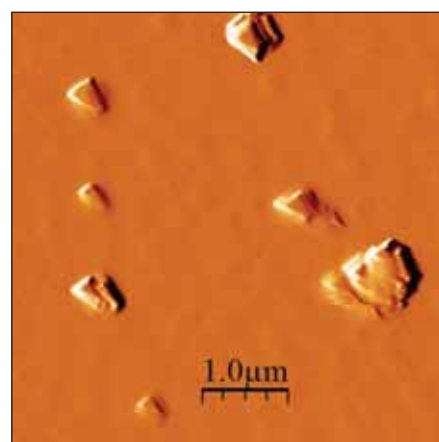


Fig. 3. Modified silicone MS-1 particles diffusion in water emulsion in order of size

mix it with bitumen. Adding MS-1 to paints gives the surface hydrophobic properties.

Gas chromatography-mass spectrometry on DFS Thermo Electron Corporation (USA) was made to determine the composition of MS-1. Ionization method: electronic discharge. Energy of ionizing electron was 70 eV, temperature of ionogen is 280 °C. Capillary column DB-5MS, length 30 m, diameter 0.254 mm, was used. Carrier was is helium. Data treatment was made with

program Xcalibur. Sample was input as a mixture with benzene in the ratio 1:100. Benzene purity was controlled by gas chromatography-mass spectrometry.

In Figs 1 and 2 you can see spectrograms of samples «hydrosil «MS-1» n/cons.» and «hydrosil «MS-1» cons.» correspondingly which were received at registration of total ion current. Identification of substances relating to chromatographic peaks of chromatograms was made by comparing of the observed mass-specters in these

peaks with mass specters of computer catalog of the equipment. Components which were not present at the catalog, were identified based on the analyses of experimental mass-spectrometer with consideration of dissipation scheme of electronic discharge.

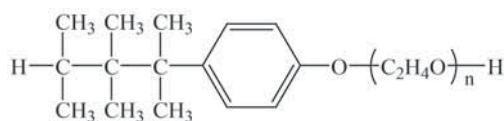
In tab.1 you can see all basic components identified by gas chromatography-mass spectrometry. Identified components are ranged in the chart below according to their amount in the composition (chromatographic peaks areas and time of exit).

Almost all the volume of the received emulsion consists of particles with the size of 320-900 nm. Average particle size is defined by statistic method at area analysis with maximal possible size of the pattern 400 nm (fig. 3). There are also larger particles with size up to 2000 nm (study with zonal microscope MultiMode V by Veeco).

Modified silicone MS-1 is not dissolved in water so our aim was to get stable 20–30% emulsion of MS-1 in water. Emulsion stability was made by introduction of stabilizer (emulsifier) into system. Non-ionic surface-active agents (surfactants) were used as stabilizer [3-5].

These surfactants were chosen because they are used in many scientific works and technological processes and are effective emulsifiers. They have a number of advantages – high heat resistance, liquid physical state at low rate of oxyethylation which facilitates dilution and diffusion in polymer containing systems, regulated level of surface activity, compatibility with components of polymeric materials.

Ethoxylated isononylphenols of AF mark produced by OJSC Nizhnekamskneftehim were used as non-ionic surfactants with variable ethoxylation degree from 4 to 12. They were purified by method given in the source[6].



Earlier in our works [7–9] we studied colloid-chemical properties of these surfactants such as wetting, adsorption, modifying effect and surface activity of the SAA. It is shown that surface activity depends on ethoxylation degree $n = 8$. Therefore ethoxylated isononylphenol with average ethoxylation degree $n = 8$ was chosen as emulsifier.

On the base of the emulsion LLC VESTO set up production of silicone-acryl water-repellent agent and paint that are not inferior to foreign competitors in terms of properties but are much cheaper. ♦

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NEWS

INDIAN COMPANY TO SET UP A FACTORY IN THE STAVROPOL TERRITORY

In New Delhi, Vladimir Vladimirov, Governor of the Stavropol Territory, and Kuldip Singh Dhingra, Chairman of the Berger Paints Board of Directors, have signed an agreement on cooperation and establishment of a paint factory. According to YUGA.ru, a preliminary agreement on this project was signed during the visit by an Indian delegation to the Stavropol Territory. Since then, the company's representatives have been studying the local market in order to determine the parameters of the project. «Implementation of the project will create at least 50 jobs. Production facilities will be phased in, while the project construction schedule is to be developed and approved by the end of this year», sources in the Governor's Press Service said.

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STUDY OF PROPERTIES OF EPOXY COATINGS FILLED WITH PIGMENTS AND FILLERS ENCAPSULATED IN POLYANILINE

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The influence of pigments and fillers, encapsulated with polyaniline (PAN) on the properties of epoxy coatings were studied. It was shown that the introduction of such pigments results in a slight decrease of glass transition temperature of coatings. It was found out that anticorrosion properties of epoxy coatings, filled with pigments and fillers, encapsulated with PAN are superior to the protective properties of the coatings, pigmented with strontium chromate.

INTRODUCTION

It is known that the polymer composite materials based on epoxy oligomers possess a high level of physical-chemical and physical-mechanical properties [1]. Epoxy oligomers are very often used for obtaining protective coatings. To strengthen the protective properties they introduce additional anti-corrosive pigments and fillers which, as a rule, are dangerous for environment, expensive and require a high degree of filling.

Currently much attention is paid to the research and development of non-toxic anticorrosive pigments, which can replace lead and chromate based pigments [2]. A promising direction in the field of pigments and fillers is obtaining core-shell pigments. Cheap unpainted fillers are used as core that is completely coated with functional shell. Core-shell pigments and fillers with polystyrene, polymethylmethacrylate as shells are also known. [3, 4]. The use of fillers and pigments encapsulated with conducting polymers, for example PAN, allows to obtain conductive pigments, possessing anti-corrosive properties [5]. Pigments and fillers encapsulated in PAN in coatings will replace toxic anticorrosive pigments such as chromates, without any decrease in protective properties, which is a topical issue in view of toughening ecological requirements to the components of the paint and varnish materials coatings. Study of properties of epoxy coatings, filled with pigments and fillers encapsulated with PAN, was the purpose of this work.

OBJECTS AND METHODS OF RESEARCH

In the studied compositions epoxy oligomer (EO) with epoxy equivalent 205 g was used as the binder. Aliphatic amine was used as hardener for all compositions. Letdown part of the composition included titanium dioxide, micro-talc, strontium chromate, non-doping PAN, chalk and core-shell pigments with PAN as shell and talc, kaolin and copper phthalocyanine as cores. All the examined materials were based on common formulation, by replacing the anticorrosive pigment - strontium chromate with other anti-corrosive pigment and chalk. All received compositions had the same PVC ≈ 41 %.

Studying of the process of curing of the compositions was performed by the gel-sol analysis [6]. The relative hardness of coatings was determined according to



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the damping of oscillations of a pendulum with the use of device TML-2142(A) according to GOST 5233-89. The glass transition temperature (T_g) of epoxy coatings was determined by thermomechanical analysis on a device TMA-500 [7]. Anticorrosive properties of the obtained coatings were determined with the use of potentiodynamic method, comparing the anodic and cathodic polarization curves, as well as counting potentials and corrosion currents on their basis [8]. Electrochemical impedance spectroscopy [9] was used for evaluation of anti-corrosion properties of coatings.

RESULTS AND DISCUSSION

Fig. 1 shows the dependence of cure rate for the used compositions. It is seen that the highest rate of increase of the content of gel-fraction is observed in compositions containing 15% of talc, encapsulated in PAN and composition containing strontium chromate + talc, encapsulated in PAN. Despite the difference in the rates of gel fraction development, its final contents in various coatings are proportionate and equal ~95% for 10 hours of curing. The difference in the rates of rise of gel fraction is probably connected with different values of the adsorption of amine hardener on the surface of anticorrosive pigments.

When studying the physical and mechanical properties of the formed coating, it was assumed that softer core-shell pigments with the shell of PAN may affect the hardness of the coating. The results of measurement of received epoxy coatings hardness are presented in table 1. As you can see, the hardness of all studied coatings is almost on the same level. The introduction of softer kernel pigments, modified with PAN, does not lead to hardness reduction.

Table 2 presents the glass transition temperature of epoxy polymer samples obtained after extrapolation to zero scan speed on temperature. As you can see, the introduction of core-shell pigments leads to reduction

of epoxy coatings glass transition temperature, compared to epoxy coatings containing strontium chromate and non-doping PAN. This is probably due to the lower density of chemical network due to decontamination of amine hardener which is spent on dedoping PAN shell. Increase of the content of core-shell pigment in the coating allows to slightly increase the epoxy coatings glass transition temperature (tab. 3).

Fig. 2 presents the results of visual anticorrosive tests of epoxy coatings, containing various anti-corrosive pigments after 500 hours of exposition in 3% NaCl solution. As can be seen, coatings containing non doping PAN, strontium chromate, talc, encapsulated in PAN, strontium chromate + talc, encapsulated in PAN show good anti-corrosive properties (Fig. 2 a, b, c, e).

Fig. 3 shows the dependences of the corrosion currents from the exposure time in 3% NaCl solution, obtained by processing the polarization curves for samples. It shows that coating pigmented with kernel pigments, after 25 days of exposure have lower corrosion currents compared to the coatings containing strontium chromate and PAN. The lowest corrosion current is observed in the samples with coating containing

Table 1. Relative hardness of coatings containing various anti-corrosive pigments

Anti-corrosive component	The relative hardness, relative unit
PAN	0,59
Strontium chromate	0,55
Talc, encapsulated in PAN	0,56
Kaolin, encapsulated in PAN	0,58
Copper phthalocyanine, encapsulated in PAN	0,63
Strontium chromate + talc, encapsulated in PAN	0,48
10 wt. % talc, encapsulated in PAN	0,51
15 wt. % talc, encapsulated in PAN	0,57

Table 2. The temperature of glass transition of epoxy coatings, filled with various anti-corrosive pigments

Anti-corrosive component	T_g , °C
PAN	38
Strontium chromate	40
Talc, encapsulated in PAN	25
Kaolin, encapsulated in PAN	28
Copper phthalocyanine, encapsulated in PAN	34
Strontium chromate + talc, encapsulated in PAN	30

Table 3. Dependence of epoxy coatings glass transition temperature on content of pigments with PAN shell (values are given for pigment with the core of talc)

The contents of core pigment, mass. %	T_g , °C
3,5	25
10	38
15	31
Strontium chromate + talc, encapsulated in PAN	30

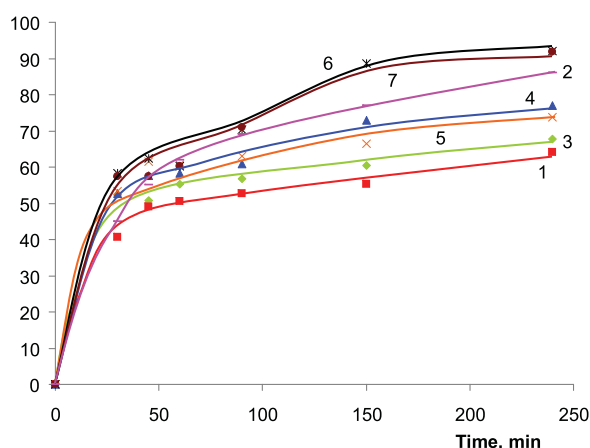


Fig. 1 – Cure rate for epoxy compositions filled with various anti-corrosive agents. Anticorrosive agent: 1 — non doping PAN; 2 — strontium chromate; 3 — 3,5 % of the talc, encapsulated in PAN; 4 — kaolin, encapsulated in PAN; 5 — copper phthalocyanine encapsulated in PAN; 6 — strontium chromate + talc, encapsulated in PAN; 7 — 15 % talc, encapsulated in PAN

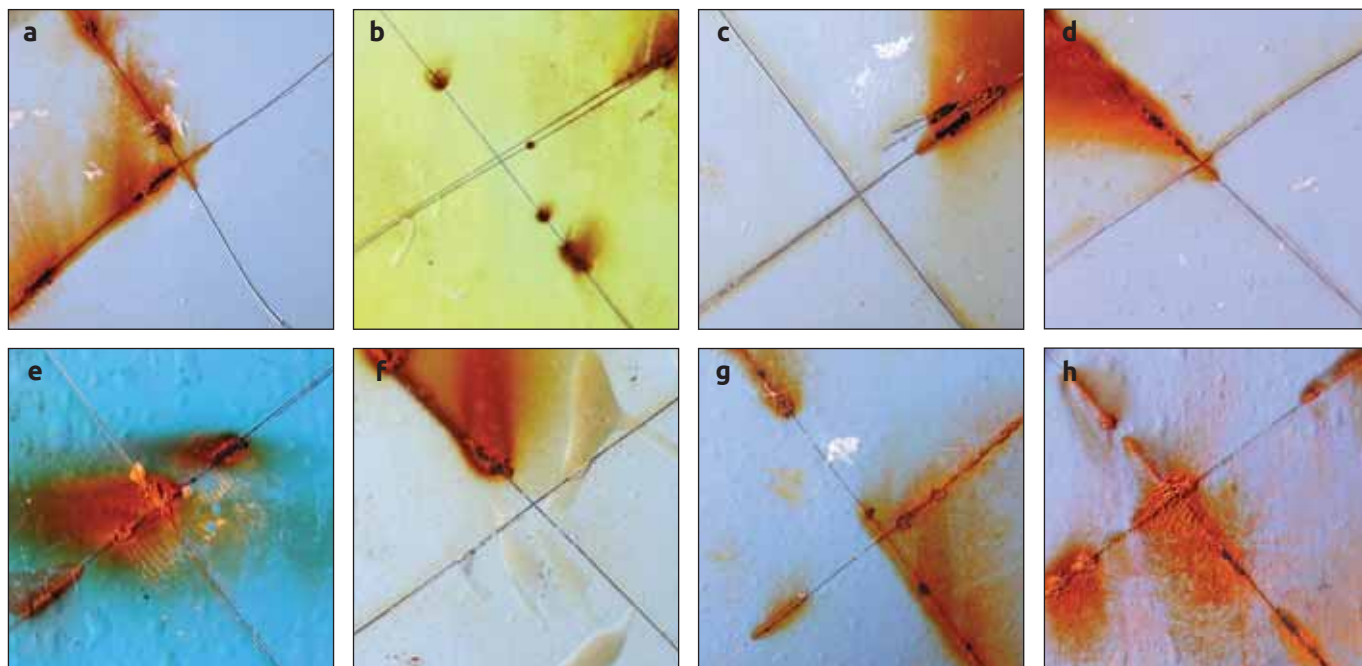


Fig. 2. Pictures of epoxy coatings, containing various anti-corrosive pigments after 500 hours of test in 3% NaCl solution. a — non doping PAN; b — Strontium chromate; c — Talc encapsulated in PAN; d — Kaolin, encapsulated in PAN; e — Phthalocyanine copper encapsulated in PAN; f — Strontium chromate + Talc, encapsulated in PAN; g — 10% Talc, encapsulated in PAN; h — 15% Talc, encapsulated in PAN

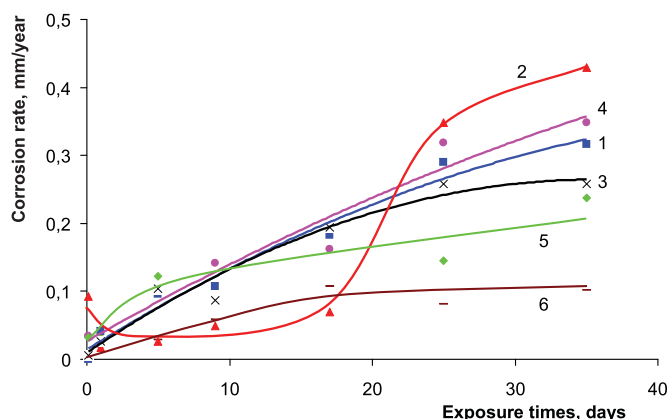


Fig. 3. Dependence of a current corrosion on time for epoxy coatings, containing various anti-corrosive pigments, in 3% solution of NaCl. Anti-corrosive component: 1 — non doping PAN; 2 — Strontium chromate; 3 — Talc encapsulated in PAN; 4 — Kaolin, encapsulated in PAN; 5 — copper phthalocyanine encapsulated in PAN; 6 — Strontium chromate + talc, encapsulated in PAN

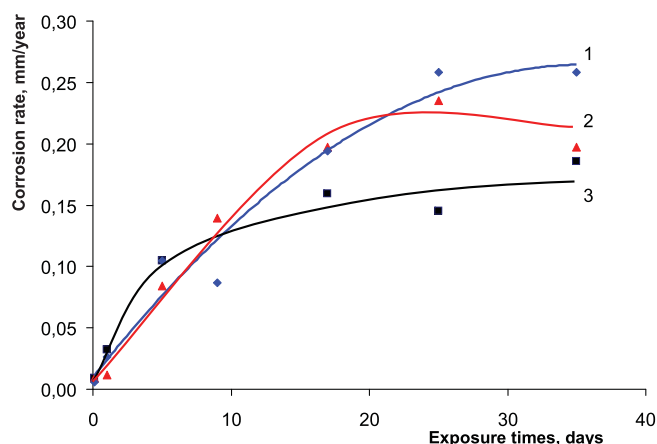


Fig. 4. Influence of the content of pigment encapsulated in PAN on the corrosion currents in 3% NaCl solution. The contents of talc encapsulated in PAN, % mass.: 1 — 3,5; 2 — 10; 3 — 15

strontium chromate + talc kernel pigment. On the basis of the above data it can be concluded that the use of kernel pigments with a PAN cover allows either completely eliminate or significantly reduce the content of toxic pigments on the basis of chromate.

Fig. 4 shows the dependence of corrosion currents on time of exposure epoxy coating samples containing different amounts of anti-corrosive pigment. It is shown that with the increase of the pigment encapsulated with PAN corrosion currents reduced. This is due to the increase of the active anti-corrosive component — PAN.

Fig. 5 (a, b) shows the spectrum of electrochemical impedance for epoxy coatings, containing PAN and

chromate strontium as anticorrosive agent, respectively. It is seen that the use of PAN as an anticorrosive agent allows increasing considerably the impedance of the obtained coatings. It is connected with reduction of permeability of epoxy coating for corrosion-active agent. This connections with the hydrophobicity of PAN complicating penetration of electrolyte in the film.

It is known that the introduction of plate particles into coating allows increasing their anticorrosive properties, by increasing corrosive agents diffusion path. When applying PAN on such particles there is an increase in the anticorrosive properties of coatings, both by strengthening the barrier effect and due to the

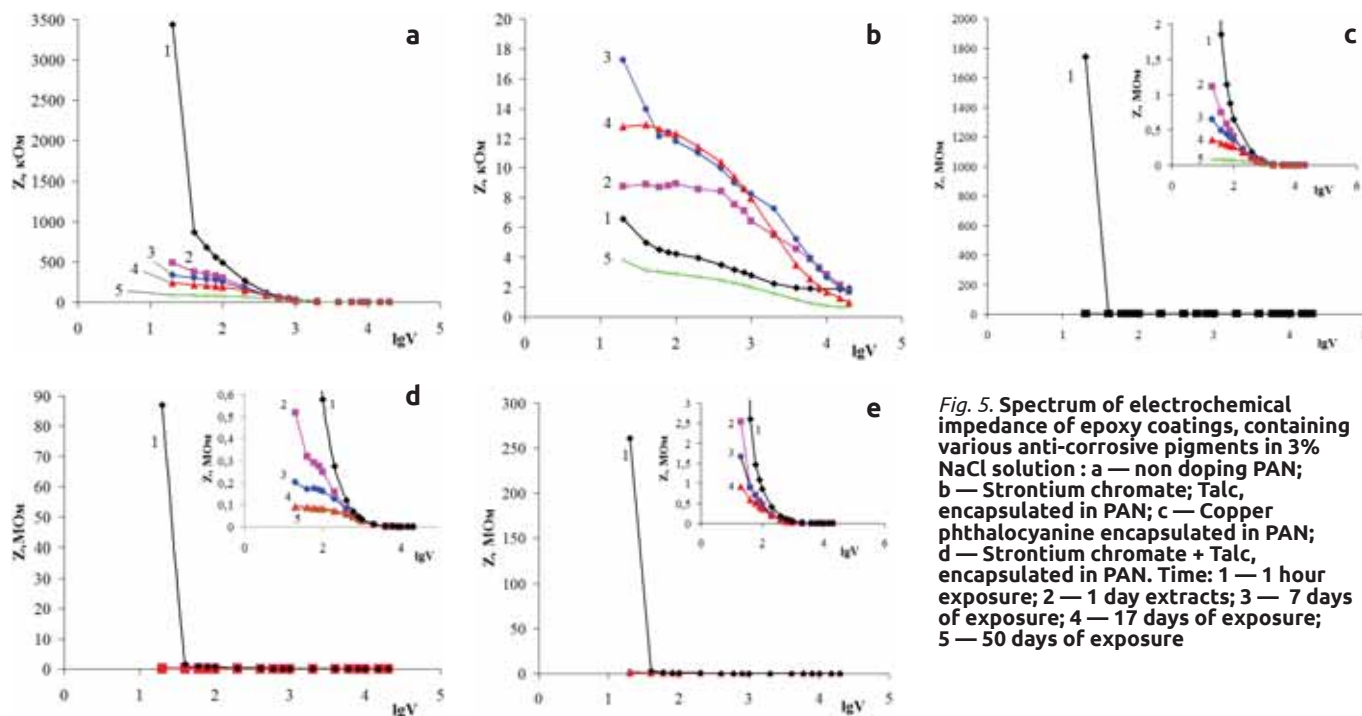


Fig. 5. Spectrum of electrochemical impedance of epoxy coatings, containing various anti-corrosive pigments in 3% NaCl solution: a — non doping PAN; b — Strontium chromate; Talc, encapsulated in PAN; c — Copper phthalocyanine encapsulated in PAN; d — Strontium chromate + Talc, encapsulated in PAN. Time: 1 — 1 hour exposure; 2 — 1 day extracts; 3 — 7 days of exposure; 4 — 17 days of exposure; 5 — 50 days of exposure

layer of PAN which increases the hydrophobicity. This explains 3–4 times higher value of the impedance of coatings containing core-shell pigments with the flake-shaped cors (Fig. 5(c and d)).

CONCLUSION

The effect of pigments and fillers, encapsulated in PAN on the curing of filled epoxy coatings has been studied. The difference in the speeds of curing of compositions with pigments and fillers modified by PAN is probably connected with different values of the amine hardener adsorption on the surface of anticorrosive pigments. It is shown that introduction of pigments and fillers encapsulated in PAN, leads to reduction of glass transition temperature of coatings. It is connected with amine hardener decontamination due to its reaction with acid anions-dopants and, as a consequence, the lower density of the chemical network. It is established that introduction of pigments and fillers encapsulated

in PAN, in epoxy coatings, allows to achieve better protective properties than properties of coatings, filled with strontium chromate, and significantly reduce the toxicity of materials. ♦

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MODIFICATION OF EMULSIFIED POLYVINYLACETATE FOR ADHESIVES AND COATINGS COMPOSITIONS

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A very special place is given to paint and coatings among all the variety of goods of industrial and household chemistry. The range of paints and lacquers is constantly updated and goes hand in hand with the search for new binders with specific properties.

Waterborne coatings is the group of materials that usually include paints, lacquers, base coats and sealant compositions based on synthetic latexes, that gradually replace solventborne materials. Environmental advantages of water-based coatings contribute to the annual growth of their production and application.

The main film-forming materials for waterborne coatings are latexes and dispersions based on emulsion polymers. This group of polymers includes polyvinylacetate (PVA), and products of its polymer transformations, which are used in thermoplastic coatings. The most widespread process of PVA industrial production is polymerisation of vinyl acetate in the emulsion (in aqueous medium) with water-soluble initiating agents and emulsifiers at the temperature of 70–85 °C for 2–3 hours.

Coatings based on PVA do not possess enough adhesion and are characterised by high film brittleness, low water-resistance and settling at storing.

To eliminate the abovementioned drawbacks, the paper suggests a method of emulsion polymerisation of vinyl acetate with glyoxal, the research of obtained polymers properties and formulating adhesive and coating compositions based on the samples obtained.

EXPERIMENTAL PROCEDURE

Emulsion polymerisation of vinyl acetate for adhesive and coating compositions was carried out using laboratory facility consisting of three-necked glass bulb with a back-flow condenser, a mechanical agitator, dropping funnels, and a helical heating mantle at the temperature of 55–60 °C and reaction time of 180–240 minutes [1]. The initiating agent was potassium persulfate, and the amount of glyoxal was in the range from 0.1 to 5.0 % (of the monomer volume).

The properties of obtained PVAD samples modified by glyoxal (PVAD_{MDG}) (Table 1) were studied using standard procedures. The settling at dilution of PVAD was in accordance with GOST (Federal standard) 18992. The relative viscosity was determined using viscosimetric technique with a flow meter VZ-246 with a 4 mm nozzle diameter. The adhesive capacity at joints was identified using a fracture testing machine RT-250M, GOST (Federal standard) 14760.

Coating compositions were prepared using a lab dissolver, i.e. a small-size unit with a built-in mixer, and an agitator with removable disks (cutters). The container was a stainless steel cup.

In accordance with GOST (Federal standard) 18992, we determined the properties of coating compositions: their exterior, drying time, settling when dissolved, and residual monomer value. We identified fineness of dispersion in the Klin in



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Table 1. Properties of PVAD and adhesive lines on its basis

No.	Glyoxal content, %	PVAD properties		Adhesive line properties	
		Settling at dissolving, %, no more than	Relative viscosity according to viscometer VZ – 246, sec. nozzle diameter of 4 mm	Durability at homogeneous pull-off, MPa	Curing time, min.
1	0	4,5	28	1,1	31
2	0,5	0,4	30	1,5	28
3	1,0	0,2	38	1,9	26
4	3,0	0	41	2,4	21
5	5,0	0	43	2,7	18

Table 2. Properties of lacquer coats samples based on PVAD_{MDG}

Parameter	Sample			
	PVAMDG 0,5%	PVAMDG 1%	PVAMDG 5%	PVA
Drying time to degree 3 at 22 ± 2 °C, min., no more than	40±0,5	20±0,5	15±0,5	60±1,0
Adhesion, grade	2	1	1	2
Relative viscosity according to viscometer VZ-243 with nozzle diameter of 4 mm, sec	45±1	50±1	55±1	45±1
Settling at dissolving, %, no more than	5	4	2	8
Fineness according to the «Klin» instrument	20±2,5	15±2,5	10±2,5	20±2,5

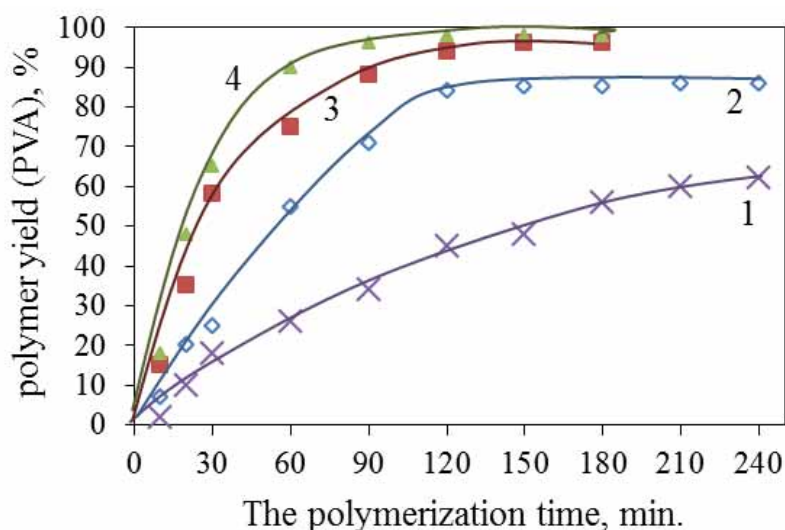


Figure – The correlation of yield polymer and the content of glyoxal: 1— (PVA); 2 — (PVAMDG – 0.5%); 3 — (PVAMDG – 1%); 4 — (PVAMDG – 5%)

strument (Grindometer-25) in accordance with GOST (Federal standard) 31973.

During polymerisation, we carried out sampling, yield of the PVA was determined gravimetrically, and correspondingly we designed correlation curves for yield polymer and glyoxal amount and synthesis time (Figure).

We can assume that the amount of glyoxal influences the polymerisation duration and polymer yield. The maximum polymer yield (calculated as vinyl acetate change ratio) is reached with 5 % of glyoxal and equates to 96–98%,

further increase of modifier content is not reasonable. The yield of vinyl acetate polymerisation without glyoxal in the following temperature range (55–60 °C) was 50 and 60% during 180 and 240 minutes correspondingly.

Table 1 presents test results, involving polymer dispersion samples and adhesive joints based on it.

To prepare coating compositions we used synthesised samples of PVAD and PVAD_{MDG} (52% solutions), 2.0% water solution of oxymethyl cellulose, titanium dioxide, calcium carbonate, aluminium flake, and marble powder as pigments and compound products. PVC for all samples was 44%.

Properties of obtained compositions and coatings on their basis are given in Table 2.

Thus, it is determined that using glyoxal as a modifying agent for the synthesis of emulsion polyvinyl acetate allows to reduce power consumption because of temperature drop and synthesis time in comparison with today technologies.

Obtained samples of modified PVAD_{MDG} as well as adhesive and coating compositions possess a high adhesion level and stability during storing. The drying time decreases.

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APPLICATION OF ULTRADISPERSED POWDER POLYTETRAFLUOROETHYLENE F-4 (FLURALIT) FOR MODIFICATION OF COATINGS ON THE BASIS OF CARBOXYLATED ACRYLIC OLIGOMERS, OBTAINED BY ELECTRODEPOSITION

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One of the ways of technological progress in the sphere of a polymer technology, including polymer coatings, is the creation of hybrid polymer materials. This can be achieved by means of introduction of ultradispersed polymer fillers to an oligomeric system. Due to such modification coatings get several new specific properties. For example, with introduction of small additives of dispersed polytetrafluorethylene, polyamide, polystyrene, penthaplast to water-based paints for coating by electro deposition, an increase of wear resistance, hydrophobicity, hardness, protective properties, chemical resistance and dispersive capacity [1-4] has been achieved. Furthermore, as a rule, the said additives were introduced to a water-based paint system in the form of water dispersion.

Today in Russia Fluralit Sintez, LLC produces powder ultradispersed polytetrafluorethylene under Fluralit trademark. It is of interest to apply this innovative product for modification of paint.

A base coat based on carboxylated acrylic oligomer for ATL-coating (Frei Lacke, Germany), that is used in OJSC AVTOVAZ (Tolyatti) in the body paint shop of automobiles under the brand name LADA Niva, was chosen as a research subject. A task of improvement of properties of coatings is critical, as the modification of the line for cathodic electrodeposition, providing better corrosion protection, requests huge capital expenses [5].

First of all, it is necessary to find the way of introduction of the water-repellent powder Fluralit to the water-based coatings. For solving this challenge the mechanism of preliminary hydrophilization of polytetrafluorethylene surface by a non-ionic surfactant was proposed. Surfactant OP-10 was used, which provides wetting of Fluralit particles, not changing the system conductivity, and due to high hydroxyl content – promotes adsorptive cooperation with the carboxylated oligomer. The latter is the necessary condition for a simultaneous joint electrodeposition of the binder and the ultradispersed polytetrafluorethylene on electrode.

Processing of Fluralit was performed by water solution OP-10 of different concentration in a bead mill within three hours. On the basis of data on kinetic system stability, determined from separation speed, a minimum concentration, wherein the most stable system was formed, composing 1% (wt), was chosen. An adsorption amount of OP-10 on the surface of Fluralit particles, which equals 75 mg of surfactant/g of powder, was determined by a weight method [6]. The Fluralit dried modified powder was directly introduced into letdown through dispersion in the bead mill



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Table 1. Characteristics of working solution of the binder for the electrodeposition

System	Concentration, c.o.,%	pH	Conductivity, mmhos/c	ζ potential, mV
ATL-korrosionfest (Frailacke)	13	9	820	-31
+ 1% (wt) Fluralit	13,5	8,8	815	-34

Table 2. Physical and mechanical properties of obtained coating

Indicators	Non-modified coatings	Modified coatings	Standard of TTM 1.94.0141-2004 OJSC AVTOVAZ
Thickness, μm GOST R 51694-2000	21-23	20-22	18-22
Adhesion, score GOST 15140-78, method 4 ISO 2409:2007	11 0		
Coating strength on impact, see on the U-2M tester under GOST 4765-73 (instead of GOST R 53007-2008)	50	50	no less than 50
Coating strength under tension on the Erichsen device, mm under GOST 29309-92	10	9,5	5, no less than
Hardness, ISO 15184	H	3H	not rated
Contact angle of wetting, $^\circ$	76	128	not rated

Table 3. Protective properties of coatings

	Non-modified coatings	Modified coatings	Standard of TTM 1.94.0141-2004 OJSC AVTOVAZ
Static action NaOH (12% solution), in 50 hours	10% bubbles	without changes	not rated
Coating resistance to exposure to salt fog in mm (corrosion exp. from a cut) on phosphate no less than - 275 h - 500 h	2	1	2, no more than
Film resistance to static action of engine oil, under ISO 2812-1:2007 method A, GOST 9.403-80 not less than - 48 h - 180 h	without changes	without changes	External appearance without changes
Film resistance to static action of gasoline Premium 95, under ISO 2812-1:2007 method A, GOST 9.403-80 not less than - 48 h - 180 h	without changes	without changes	External appearance without changes

within three hours. An obtained composition was used for preparation of a test sample of an electrodeposition bath. For comparison the control sample was made of an initial non-modified paint. Table 1 shows characteristics of the samples.

The electrodeposition was performed on degreased steel plates in a laboratory bath in a potentiostatic mode ($U = \text{const}$). Optimal parameters of the electrodeposition were: voltage — 180 V, duration — 120 s, temperature — 250 °C. A hot-cure was performed at a temperature of 100 °C within 20 minutes. Coatings in both cases were without defects, smooth, uniform.

Properties of the coatings were studied by standard methods, accepted in paint industry in compliance with standards of TTM 1.94.0141-2004 of OJSC AVTOVAZ.

Table 2 shows physical and mechanical properties of coatings and wetting angle (determined by a «still drop» method).

Table 2 shows that the modification results in increase of hardness and hydrophobic properties of the coatings.

Protective and anticorrosion properties of the coatings were determined through testing:

Moisture resistance according to GOST 9.403-80 method A (results are shown in Table 3);

oil and its derivatives resistance according to GOST 9.404-88 (results are shown in Table 3).

The results show that the modified coatings have better water resistance and salt resistance in comparison with the non-modified coatings, when other properties remain unchanged under the static influence of liquids.

Therefore, the ultradispersed Fluralit can be used for improvement of properties of electrodeposition coatings on the basis of the carboxylated acrylic binder. The preliminary processing of the Fluralit surface by the nonionic surfactant is necessary. In comparison with other results, obtained in modification of similar coatings by a water dispersion of fluoroelastomer F-4DV, introduced to the system directly to the working solution of the bath [4], half the amount of the Fluralit is necessary to achieve positive results.

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THE ONE COMPONENT PAINT FOR BRICK AND CONCRETE SURFACE ON THE BASIS OF THE LIQUID POTASSIUM GLASS PRODUCED BY JSC «DOMANOVSKIY MANUFACTURING AND TRADE PLANT»

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The main function of exterior paints is to protect the building from the destructive effect of environment. To prolong building's life one must protect it with state-of-the art silicate paints which are ecologically friendly. IGIC NAS of Belarus (Minsk) developed protective single-component paint for mineral substrates on the basis of the liquid potassium glass produced at JSC «Domanovskiy Manufacturing and Trade Plant» for substitution of imported materials, reducing the cost without compromising the performance.

Exterior paints should protect the building from the damaging effects of the environment in addition to creating decorative effect. The main causes of the destruction of buildings facades are defrosting (i.e. the effect of low temperatures), the effect of mineral salts and fungi, mosses, lichens and algae.

Silicate facade paints are state-of-the art, ecologically friendly, intended for external and internal use on mineral substrates (brick, concrete, plaster). They are used for refinishing residential, commercial, industrial buildings, warehouses, special objects, for example shelters, water towers, underground passages, etc [1]. Silicate paints compared with acrylic coatings are less elastic and do not seal small cracks in the foundation. In addition, they are less water-resistant, so during heavy rains water can penetrate walls. However, silicate paints have high vapor permeability, which allows water to evaporate very quickly after the rain. Due to this property old buildings, the walls of which are poorly protected from the rise in groundwater, are very often painted with silicate paints. Silicate paints are also quite reasonable choice for painting walls, exposed to increased moisture inside the building. An important property of silicate paints is that they do not provide environment for the growth of microorganisms and therefore do not require special additives.

Two-pack silicate paints are compositions consisting of water solution of liquid glass (mainly potassium), mixed with solids (alkaline mineral pigments and fillers) immediately before use [1, 2]. It should be noted that use of liquid glass in two-pack silicate paints requires separate purchase and storage from other components due to high chemical activity. Consequently, the main disadvantage of two-pack silicate paints is the need for thorough mixing of both components in situ and limited pot life.

The above mentioned problems are solved by adding polymer water dispersions in two-pack silicate paints [3-9]. Advantages of one-pack water-based silicate paints containing hardener-silicatizator, is storage stability for a long time and



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possibility to apply in single pack version. These paints contain alkali-resistant dispersion of synthetic resins in water, as saponification products can react with liquid glass and lead to thickening of paint during its storage. Due to the presence of polymer water dispersion, film-formation and production technology of these paints is special: they must be produced according to the technology of water-dispersion paints with the addition of many components typical for WD paints.

One-pack silicate paints are currently being produced in many foreign companies, for example, ALCRO-BECKERS AB and VIVACOLOR (Sweden), ALLIGATOR and CAPAROL (Germany), JUB (Slovenia), TIKKURILA (Finland), and others; they are recommended for use in construction in the Republic of Belarus and in the CIS countries. Known compositions of this type of paints are patented in the Russian Federation [7-9]. However, these paints have a limited shelf-life not exceeding 6 months.

It should be noted that when formulating one-pack water dispersion silicate paints special attention should be paid to the choice of pigments and fillers. It is known that pigments and fillers fall into inactive and active according to their ability to interact with liquid glass [1, 2]. Inactive pigments — TiO_2 , Cr_2O_3 , ultramarine, carbon black, phthalocyanine green, blue and others.

Bright shining white silicate paints can be obtained using titanium dioxide. Titanium dioxide is poorly soluble in alkalis [10]. It occurs in nature in three crystalline modifications: brookite, anatase and rutile. Rutile forms of the light and weatherproof. As a rule, to improve the processibility titanium dioxide is subjected to surface treatment by organic materials. Some of these materials react with the liquid glass and are prone to saponification. This can lead to deterioration of stability during storage and silicate paint thickening. Therefore, titanium dioxide of rutile modification treated with inorganic materials is more preferable. Main active pigments — ZnO , yellow iron oxide pigment, ochre, and others. At the same time active pigments and fillers act as hardener [1, 2, 10].

Filler is one of the most important components in paints production; they are insoluble mineral substances added in tinted compositions for reducing the amount of pigments needed and give coatings properties such as durability, heat-, acid-, alkali resistance, gloss and other characteristics. As inactive fillers for silicate paints one can use chalk, mica, talc, aerosil, as active - dolomite, marshalite, alumina and others [1, 2]. Chalk due to its high adsorption properties ensures the uniformity of structure of paint and prevents delamination. It is subject to very slow alkaline hydrolysis resulting in the formation of calcium hydroxide and carbonate ion. Addition of catalysts, in particular, calcium borate, which is the carrier of calcium ions in the solid phase of the solution for formation of deposited hydroxide, can significantly accelerate the rate of alkaline hydrolysis of chalk. Therefore, in this system, calcium borate is highly active hardener-silicatizator, it is introduced in two-pack silicate paints in quantities of less than 1 wt. %.

Silicate fillers such as kaolin, ground mica and microtalc are a preferable choice for filling silicate paints as they build in the net structure in the process of silicization more easily than other fillers due to their affinity to liquid glass.

Kaolin is a colloquial name for mineral product, fully or partially consisting of aluminosilicate of kaolinite, the structure of which can be described as a layer of silicon rings, bound with a layer of octahedra of aluminium with oxygen atoms. With its high hydrophilicity, kaolin improves flow and retards evaporation of water from the film [2, 10], contributing to the smooth process of gelling and building high-quality coating.

Mica (muscovite) is practically the only filler with flake particles that keep their shape even after strong grinding [2, 10]. Lamellar particles of micromica distributed in layers above one another improve levelling, as scales slipping one on another create lubricating effect. Particles of mica reduce coatings permeability and increase mechanical resistance. In other words, ground mica increases coatings durability, reduces the tendency to cracking under the influence of temperature and, furthermore, it inhibits the formation of dense sediment during storage.

Microtalc due to its physicochemical properties is a hydrophobic filler, it provides high weather resistance, heat resistance and chemical resistance (in whole decomposes only in hydrofluoric acid), has a high dielectric and adsorption properties. The lamellar form of talc particles reduces the permeability of coatings, fibrous particles increase resistance to the formation of bubbles during the film-forming, as well as sedimentation stability. Talc in alkaline liquid glass is exposed to hydrolysis with the formation of hydrate of magnesium oxide. However, the rate of hydrolysis reaction is rather slow.

It should be noted that so far in the Republic of Belarus domestic production of one-pack silicate paints was not an issue. The main reasons are the lack of own original developments in this field, as well as the poor use of ingredients on the basis of domestic raw materials, for example, liquid potassium glass which is the dominant product on the market of alkali silicates in Belarus and in the CIS countries and is manufactured by JSC «DOMANOVSKIY MANUFACTURING AND TRADE PLANT».

Institute of general and inorganic chemistry of the National Academy of Sciences of Belarus starting from 2009 works on the development of compositions of protective and stabilizing coatings for multifunctional applications. In the result of research was developed single-pack silicate paint, which is a composition consisting of liquid potassium glass (GOST 18958-73) produced by JSC «DOMANOVSKIY MANUFACTURING AND TRADE PLANT» (table 1), inactive, alkali-resistant fillers and pigment (titanium dioxide), WD polymer and auxiliary substances (dispersant, thickener, defoamer), stable at high pH, and also the special additives, that contribute to double silicification of silicate coatings and giving their surface hydrophobicity («Lotus effect»).

Table 1. Physical and technical characteristics of liquid potassium glass produced at JSC «DOMANOVSKIY MANUFACTURING AND TRADE PLANT»

Appearance	Dense liquid of yellowish or greenish (greyish) color
Silica module	2,5–4,0
Density, g/cm ³	Not less than 1.3
Method of storage	Store in tightly closed container at a temperature not less than –5 °C
Warranty period of storage	12 months from manufacturing date

Table 2. The basic properties of one-component silicate paint and coatings based on it

№	Name of indicator	Value of indicator
Paint		
1	Solids content, %, not less	45
2	Degree of grinding, mm, not more	70
Coating		
3	Opacity, g/m ² , not more	210
4	Drying time to degree 3 at 20 (±2) °C, h, not more than	1
5	Period of silicatization, h, not more than	8
6	Conditional lightfastness (changing the coefficient of diffuse reflection), %, not more	5
7	Adhesion, MPa, not less	0,8
8	Coefficient of water-vapor permeability, mg/m * h * Pa, not less	0,013
9	Resistance to static action of water at 20 °C, hours, not less	24
10	Resistance to influence of variable temperatures, cycles, not less	10
11	Frost resistance, cycles, not less	50
12	Resistance to influence of climatic factors, cycles, not less	100

Physical and technical characteristics of liquid potassium glass, corresponding to GOST 18958-73 are presented in table. 1.

Studies have shown that the content of the WD polymer in paint optimal composition should be not more than 2 wt. %, silicate binder - not less than 25 wt. %.

The paint is prepared by grinding the components on VAS ZMPR with shaft rotation speed of 1200 rpm for 1 H. Paint was applied to the dry concrete surface with a brush, roller or airless spraying in two layers with intermediate drying for 1–1,5 hours at a temperature of 18–20 °C. At lower temperatures or high humidity of the drying time may be extended to 24 hours

The following technical and technological properties of paints and coatings based on it were investigated:

- degree of paint grinding on grindometer «Klin» according to GOST 6589, method B;
- drying time to degree 3 according to GOST 19007;
- adhesion of the coating to the substrate according to GOST 28574;
- nonvolatile substances content according to GOST 17537, method 1;
- opacity according to GOST 8784, method 1;
- vapor permeability coefficient according to STB 1263;
- resistance to static action of water according to GOST 9.403, method A;

- conditional lightfastness according to GOST 21903, method 2;
- resistance to influence of variable temperatures, according to GOST 27037;
- frost resistance according to STB 1263;
- resistance to influence of climatic factors according to GOST 9.401, method 2 (3);
- period of silicatization according to GOST 18956.

The basic operational characteristics of single-component silicate paint and coatings based on it are given in table 2.

It should be noted that in the course of testing of resistance to the effects of variable temperatures, static action of water and climatic factors, the coatings retained their integrity; there was no cracks, bubbles.

By its physico-chemical and technological properties developed paint corresponds to the standard TU BY 100029049.082-2011 «Silicate Paint». As a result of toxicological-hygienic researches of paint obtained certificate of the state sanitary-hygienic expertise № 16-12-04/4464-4465 from 02.08.2011.

Warranty period of storage of a paint of not less than 12 months from the date of manufacturing.

The developed single-pack silicate paint provides the diffusion of water vapor, gives the coating water-repellent properties, demonstrates good physical and mechanical properties and optimally protects the surface from moisture. Because the paint is import substituting and competitive in quality and cost, it will undoubtedly take its niche in the construction markets of the Republic of Belarus and CIS countries. ♦

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COLLOID-CHEMICAL PROPERTIES OF THE UNCURED COMPOSITION OF PROTECTIVE-DECORATIVE COATING

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INTRODUCTION

Coatings consist of two main components: the liquid phase, consisting of a film-forming or film-binding substances (which are identical concepts in the domestic terms) and solid phase, which consists of pigments, fillers and other. Film-forming substances of coatings are designed to bind the pigment particles together and to create solid and durable film well adherent to the substrate.

Legislative restrictions concerning the use of organic solvents forced paint manufacturers to revise the formulations of materials to reduce VOC.

The results of the survey conducted by Symbol-Marketing agency show that construction and trade organizations mostly buy primers, water-dispersion paints and enamels [1]. These coatings are used by more than 90% of organizations involved in repair and construction works. Russian manufacturers are focused mainly on the production of organic paints and enamels and are not capable to fully satisfy the demand for water-based coatings. Naturally, almost one-third of water-based coatings in the Russian market are imported. The segment of water-based coatings has great potential for growth, currently the share of this type of products in the structure of the Russian market of coatings is significantly lower than the world average. In 2005 water-based coatings accounted for approximately 60–70% of the global market of coatings.

The total volume of coatings market in Russia, according to the data of interregional association «System of inter-regional marketing centers», equals 700–750 thousand tons, according to Goskomstat — about 1000 thsd tons [2]. The market volume continues to grow.

Organic components (binders and solvents) are toxic to humans during synthesis, paint production and application. Organic coatings, for example, epoxies, have low resistance to microbiological impacts [3], they are flammable and explosive. They are comparatively non-durable: in most common cases, when the painted surface is cleaned mechanically in the open air, the service life of coating on organic film-former is 1–2 years [4].

As for water-based paints, with polymer as binder, primarily latex and silicone resins, they have a low resistance to abrasion, and are not recommended for use on metal surfaces. Another significant drawback of pure silicate paints is double packaging, which means that pigments and binder come in different packages and must be mixed before applying. Paint, after mixing, should be used within a short period of time specified by the manufacturer. Components of the paint are mixed during 30–40 minutes in a bead mill, together with the required amount of liquid glass. The mixed paint is filtered through a sieve, poured in metal cans and delivered to the premises where it is applied within 12–24 hours [5].

A task of this research is to create non-toxic, non-combustible, water-based, one-package paint.

This study presents experimentally established dependency of wetting angle and surface tension in uncured composition of protective-decorative coating based on



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nanodispersed hydrosilicate potassium and latex (dispersion acrylic-methacrylic ester polymer).

THEORETICAL ASPECTS

Binder quality is characterized by such key indicators as viscosity, surface tension, presence of volatile and non-volatile substances, the presence of gels and microgels, particle size, colloid stability, adhesion strength. These characteristics define the viscosity of paint, durability and hardness of coating.

The magnitude of the surface tension of varnishes' and paints' uncured binders depends on the nature of solvents. Currently the most common solvents are organic (aromatic and aliphatic hydrocarbons, esters, alcohols, ketones), for which the surface tension varies $\sigma = 22\text{--}36 \text{ MJ/m}^2$. Increasing concentration of solvents leads to diminishing surface tension of uncured paints, most significantly when solvents themselves are of low surface tension kind. The highest values of surface tension are attributable to water-based coatings, because the surface tension of water is much higher than that of organic solvents: $\sigma = 72,7 \text{ MJ/m}^2$. Waterborne paints insufficiently wet hydrophobic and poorly cleaned substrates. The ratio of the values of surface tension of binder and solvent is of great importance in the process of film-forming. Alcohols and surface-active agents (surfactants) are added to reduce the surface tension of waterborne paints. The presence of non-ionic surfactants has a positive effect on the surface activity of non-aqueous paints. Surfactants can simultaneously adjust other properties of paints: rheological, electrical (the ability to charge in electric field), stability (lack of stratification) during shelf-life.

Adhesion, wetting and levelling are interphase interactions that occur between condensed phases. The phenomena of wetting and levelling are closely connected with adhesive and cohesive forces. Adhesion is a molecular attraction between two surfaces of heterogeneous solid or liquid phases in contact. Adhesion is the reason for bonding of two different substances by physical or chemical intermolecular forces. The work of adhesion W_A is calculated by the Young–Dupré equation [6] on the basis of experimental values of surface tension on the boundary of liquid and gas (σ) and wetting angle (θ):

$$W_A = \sigma \times (1 + \cos \theta) \quad (1)$$

It is known that the adhesive force of coatings correlates with the work of adhesion [7].

Cohesion is the sticking of parts of one and the same homogeneous body (liquid or solid). Cohesion is due to the chemical bond between the particles of the body (atoms, ions) and intermolecular interaction. Work of cohesion is determined by the amount of energy spent on the reversible isothermal break of a body on the cross section, which is equal in size to a unit of surface, because when broke the surface splits into two parts; cohesion work is equal to the surface tension on the boundary with gas multiplied by 2 [6]:

$$W_K = 2\sigma \quad (2)$$

Wetting and levelling are of great importance. Wetting angle characterizes the contact interaction of paint and solid surface. Work of wetting is calculated by the formula [8]:

$$W_{CM} = \sigma \times \cos \theta \quad (3)$$

Wetting (wetting coefficient S) is quantitatively characterized by a cosine of wetting angle, and is determined by the ratio of work of adhesion to work of cohesion for wetting liquid (relative adhesion):

$$S = W_A / W_K = (1 + \cos \theta) / 2 \quad (4)$$

Levelling is an important technological parameter, because shine, smoothness of the surface, the presence or absence of craters, shagreen depend on this parameter. This parameter is characterized by a levelling coefficient:

$$f = W_A - W_K = \sigma \times (\cos \theta - 1) \quad (5)$$

As to the levelling of liquids on solid substrate, the levelling coefficient can't be positive, because of $\cos \theta - 1 < 0$.

EXPERIMENTAL PART

Binder consists of inorganic and organic components.

As inorganic part of the binder we used the aqueous solution of nanodispersed potassium hydrosilicate (MONOSIL K, produced by «EKOHIM SPB» LLC), with a concentration of 33,3% wt. and silicate module of 3,48. According to the works [9-13] liquid glass is a typical nanodispersed system.

As the organic part of the binder we used latex dispersion NOVOPOL 004A (produced by LLC «Group «HOMA»»), which is the dispersion of copolymers of esters of acrylic and methacrylate acids. This dispersion is recommended for the production of anticorrosive primers for the ferrous metals, ground-enamels for the ferrous metals, base coats on ferrous and nonferrous metals [14] (table 1).

Were prepared the solutions containing aqueous solution of nanosized potassium hydrosilicate (PHS) and latex dispersion NOVOPOL 004A (table 2).

For definition of the surface tension we used the stalagmometric method (the method of counting falling drops) [8]. The essence of the method of counting drops is in measuring the mass of the droplets formed upon discharge from the spout of the stalagmometer. Slow stream of fluid out of the hole or from a vertical tube forms a drop; the time of formation of drops should be from 5 to 20 seconds. Separation of drops occurs on the neck or waist, the radius of which is smaller than that of the hole. It is assumed that at the time of separation the force of surface tension is equal to:

$$F = 2\pi \times R \times \sigma \quad (6)$$

where R is the radius of the hole from which drops fall, σ is the surface tension of the liquid.

And at the same time, the force of surface tension is equal to the force of gravity

$$P = m \times g, \quad (7)$$

where m is the mass of a single drop.

i.e.

$$2\pi \times R \times \sigma = m \times g. \quad (8)$$

Accurate measuring of the radius of the hole is almost possible, therefore, conventionally they resort to the com-

Table 1. Technical characteristics of NOVOPOL 004A dispersion

Contents of nonvolatile substances, wt. %	44-46
Density, g/cm ³	~1,04
pH	7-9
Minimum temperature of film formation (MTFF), °C	22-25
Brookfield viscosity at 20 °C, RVT/2/20, mPa·s	150-600
Conditional viscosity according B3-4 at 20 °C, c	14-30
Particle size, mkm	0,1-0,15

Table 2. Composition of film former

№ of composition	The content of PHS, mass%	Content of NOVOPOL 004A dispersion, wt %	Designation of composition	Notes
1	0	100	L	
2	10	90	1-9L	Thick clotted gel
3	25	75	1-3L	Homogeneous solution
4	50	50	1-1L	
5	75	25	3-1L	Settling in 2-3 hours
6	90	10	9-1L	
7	100		K ZhS	

Table 3. The cosine of the wetting angle ($\cos \theta$), surface tension (σ), adhesion action (W_A), cohesion action (W_K) and wetting action (W_{CM}), coefficient of wetting (S) and spreading (f) for different compositions of film formers

Composition	$\cos \theta$	σ , mN/m	W_A , mN/m	W_K , mN/m	W_{CM} , mN/m	S	f , mN/m
L	0,541	25,1	38,7	50,2	13,6	-11,5	0,771
1-3L	0,675	40,8	68,3	81,6	27,5	-13,3	0,838
1-1L	0,746	49,9	87,0	99,8	37,1	-12,8	0,872
3-1L	0,752	63,2	110,8	126,4	47,6	-15,6	0,877
9-1L	0,771	83,5	147,9	167,0	64,4	-19,1	0,886

parative method. If we know the surface tension of the standard liquid, such as water, then we put the equation down as follows:

$$\sigma_0/m_0 = \sigma_1/m_1 = g/(2\pi \times R) = \text{const}, \quad (9)$$

where σ_0 , σ_1 – the surface tension of the water and the investigated liquid, respectively, m_1 and m_0 – weight of one drop of water and of the investigated liquid, respectively.

Error of the method is 10%.

The wetting angle was determined by still drops method. The essence of the method is that a drop of uncured binder is placed with the help of thin tube on a hard flat substrate, the height (h) and base width (w) of drops of the liquid under investigation is then measured.

During the study we used the projector that helped create a larger drop image, on which the necessary measurements were made. The cosine of the wetting angle was calculated according to the equation:

$$\cos \theta = [(d/2)^2 - h^2] / [(d/2)^2 + h^2] \quad (10)$$

Error of the method is 10%.

The test formulations were applied to the plates from ferrous metal cleaned from rust.

RESULTS AND DISCUSSION

Table 3 presents the experimental data obtained by definition of the wetting angle and surface tension of binders, calculations for work of adhesion of binders to the substrate, work of cohesion and wetting, and also factor of wetting and levelling of different compositions of binders.

The data show that increasing the nanodispersed potassium hydrosilicate volume and decreasing the share of the latex dispersion causes strengthening of the adhesion of the binder to the metal substrate, as well as improving wetting and levelling. Unfortunately, the resistance of some compositions (3-1L, 9-1L) is low. The work on the selection of dispersers and emulsifiers that will help to solve this problem is currently underway.

Currently the market price of liquid potassium glass is 1,5–2 times lower than the cost of latexes, so we consider it appropriate to introduce the aqueous solution of nanodispersed potassium hydrosilicate into the formulation of water-based paints.

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INFLUENCE OF MATTING ON THE COLOUR OF POWDER EPOXY-POLYESTER COATINGS

Daria S. Kotova, Eugene A. Indeikin

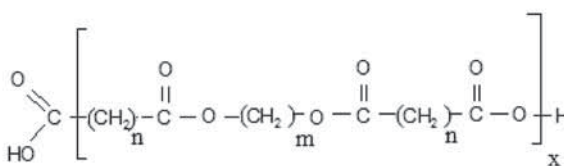
Yaroslavl Powder Coatings Plant, Yaroslavl State Technical University

Powder coatings application is a modern industrial technology to provide high-quality durable coating with excellent performance and decorative properties on metal, glass, ceramics, as well as some types of plastics.

Epoxy-polyester materials are the most common in powder coatings technology. They are obtained through a combination of epoxy and polyester (carboxylated) oligomers and therefore often named hybrid systems. Wide curing temperature range is possible with adding suitable catalysts in composition. The presence of two different binders results in coatings with intermediate properties. Their corrosion resistance approaches the epoxy, but solvents and alkalis resistance is lower. On the other hand, unlike epoxy, their weather resistance is better. Decorative properties of epoxy-polyester coatings are more lasting [1].

Demand for coated products with a reduced reflectivity has increased recently. Such coatings have an original appearance and can hide the defects of the coated surface. But the properties of polymer coating composition has a significant change in the transition from matt to glossy surface [2]. It is very necessary to study the influence of matting on the properties of epoxy-polyester powder systems and, first of all, optical properties.

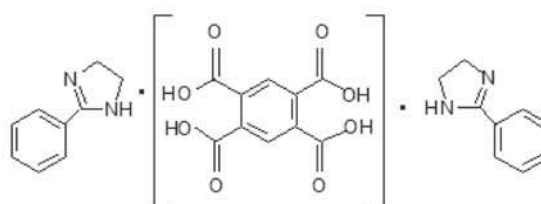
Polymer components in hybrid powder coating is a mixture of binders: saturated carboxylated polyester resin



and a solid epoxy oligomer



which is the reaction product between liquid epoxy resin and bisphenol-A. As the matting agent we used 4,5-digydro-2-phenyl-1H-imidazole-1,2,4,5-benzotetracarboxylate.



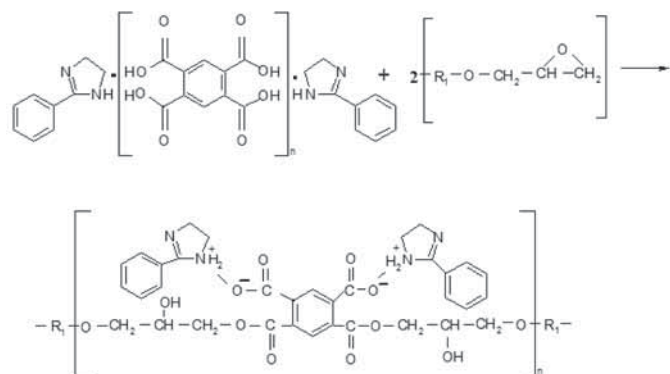
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To regulate the properties of the obtained coatings we used as additives:

- levelling agent — to improve the levelling and reduce orange peel effect — silicon dioxide, modified polyacrylate.

- de-aerating additive for powder coatings is used as a degassing agent — (2-hydroxy-1,2-diphenyletanon).

The reaction between the matting agent with an epoxy oligomer:



The rate of reaction of the carboxyl groups with the epoxy crosslinking agent is higher than with polyester, because of the catalytic action of imidazole ring having a basic nature and bound in the form of salts with pyromellitic acid. Furthermore, the acid reacts better with

the oligomer due to a greater mobility than the units of the high molecular compound. Matting is realized due to the rapid formation of cross-linked epoxy resin which is incompatible with epoxy-polyester the formation of which occurs later.

Matting associates with light scattering by surface and it is caused by surface topography, emerging as a result of epoxy resin particles formation — a reaction product of the epoxy oligomer with matting agent [3,4]. As shown in the pictures taken at microscopic research, this interaction leads to the appearance of aggregates in epoxy-polyester matrix. Their aggregates are incompatible with polymer and have crystalline structure (Fig.1).

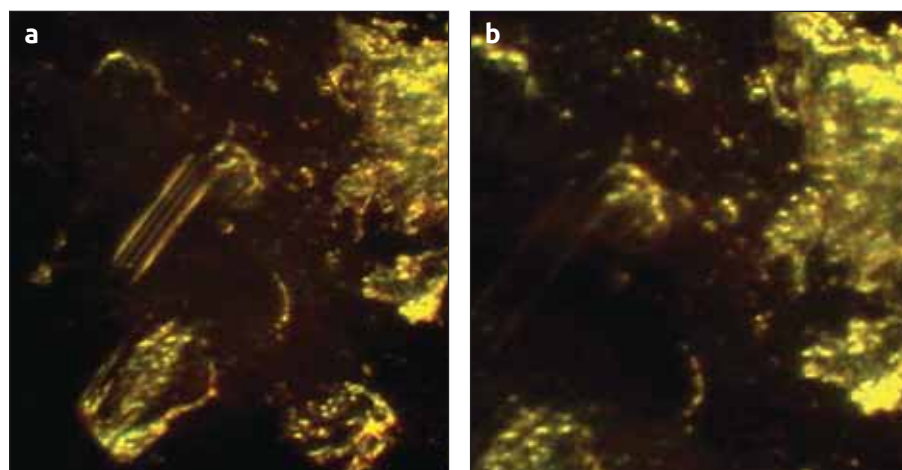
The crystalline nature of the particles formed of epoxy resin is confirmed by micrographs of matt coatings in polarized light and crossed polarizers (Fig. 2). The surface relief is formed by aggregates composed of mono crystals of polyepoxide.

In order to study the process of matting we selected polymer powder coatings, approximately corresponding to the three primary color valences (red, blue and green) and achromatic — black and white, and studied the influence of the matting agent on the structure and optical properties of the polymer layer.

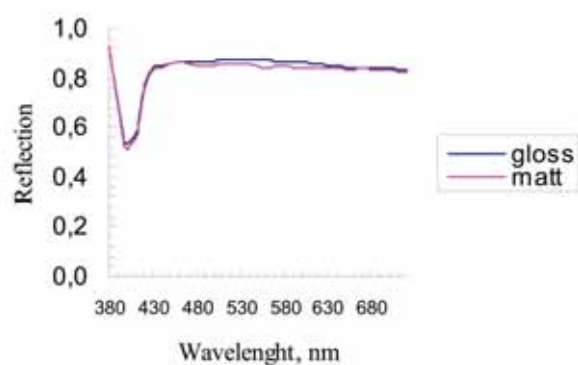
Coatings have been formulated and manufactured with 5% wt. of matting agent, the gloss in the clear coat from 20 to 30%. The process of producing coatings was three-stage: premixing (dry blending), extrusion (melt



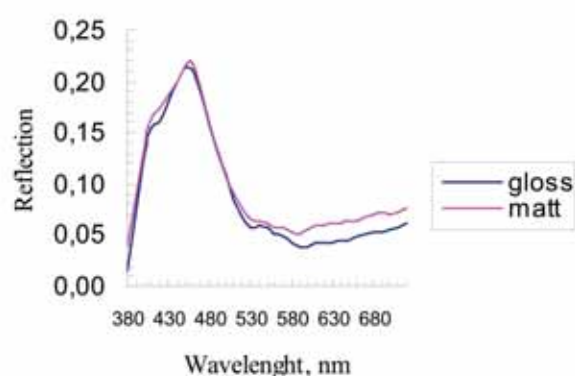
Picture 1. Epoxy-polyester coatings. a — glossy coating on the steel surface, b — content of matting agent 1,5 %, c — content of matting agent 7%



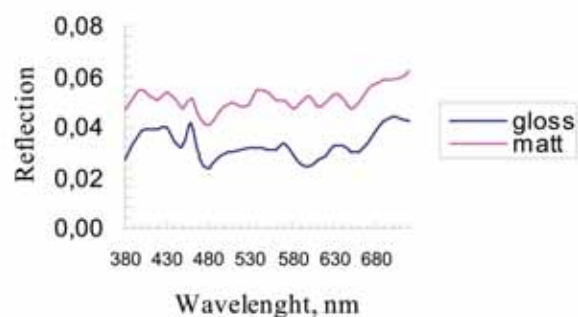
Picture 2. Micrographs of crystal and epoxy resin aggregates, magnification 3000x. a — in polarized light, b — crossed polarizers



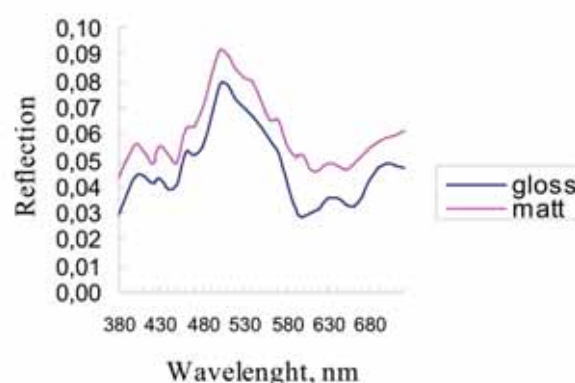
Picture 3. The spectra of diffuse reflection for white coating



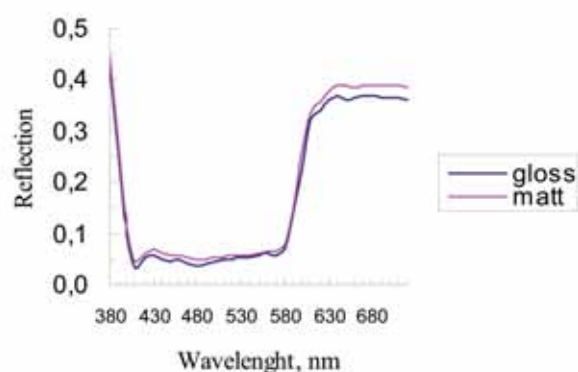
Picture 6. The spectra of diffuse reflection for blue coating



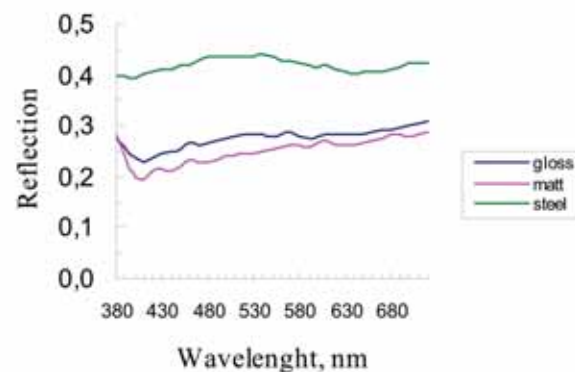
Picture 4. The spectra of diffuse reflection for black coating



Picture 7. The spectra of diffuse reflection for green coating



Picture 5. The spectra of diffuse reflection for red coating



Picture 8. The spectra of diffuse reflection for clear coating

blending), grinding and sieving of the extrudate. Curing conditions: 15 min. at 180 °C.

Matting crosslinker introduction led to the expected reduce of gloss, but also it changed the color depending on the color valency.

Reflection coefficient decreased with the matting in the wavelength range from 460 to 590 nm with a maximum variation for 490 nm. This change in reflection coefficient is observed in the range of wavelengths most receivable by human eye. Such change in the spectrum the eye perceives as darkening. Based on Rayleigh theory the reflection coefficients in the short- or long-wavelength part of the spectrum are expected to decline with the increasing number of scattering centers in coatings

[5]. It is typical for solvent-based and water-based matting materials. Deviation from this pattern in the case of powder materials is due to the fact that the matting mechanism is not determined by introducing inorganic matting filler, but by forming a heterogeneous polymer matrix. For conventional white enamels curve of reflection shifts to the right with matting, in case of powder coatings the reflection rate goes down throughout the whole range of wavelengths.

Matting associates with a change of the surface structure [6]. The black glossy coating reflects light without diffusion and scattering. In the case of matt coating adds a significant amount of scattered light due to the microscopic inhomogeneities of polymer surface.

Table 1. Change of the Kubelka-Munk function for selected wavelengths in the transition from glossy to matt surface

Color	λ , nm	ΔF
White	600	-0,0037
Black	600	11,0382
Red	650	0,0784
Blue	650	3,3277
Green	600	8,0476

The cause is in the difference in the refractive indices of the polymer and air.

In the case of red coating varies only illuminating power with no apparent bias of hue.

For blue coating the change has occurred in the long-wavelength part of the spectrum, which is exactly in the absorption area.

For green coating as for black, there is a parallel change in the spectrum characteristics.

In the case of clear coating reflection coefficient decreases and matt coating has a yellowish tone.

The demonstrated specters show that coatings formed from powder materials don't have spectral shift observed in the wavelength axis. However, there is a change in hue, especially significant for achromatic coatings. For the introduction of correction to determine the influence of changes in the pigment content to color change in a matt finish coatings were conducted a series of studies. Color and achromatic pigments ratio changed within a small range. Estimation was based on the two constants of Kubelka-Munk theory. For this purpose, the values of the Kubelka-Munk function for wave-lengths were corresponded to the maximum reflection coefficient with matting [8].

Corrections to the concentration of the chromatic pigments mixture in the transition to a matt system were calculated to obtain new coatings on the updated formulations. For black and red coatings for the regularity verification were made formulations with a deviation from the original in the larger and smaller lightness.

It was found, that the generally spectrum displacement is in the required direction with formulation correction. But full combination with gloss coating is not observed. This is due to the fact that we have adopted the calculation with only the gross content of color pigments. Besides the introduction of a matting agent, forming the scattering centers, and the inorganic filler presence causes the summation of the light fluxes for scattered light.

CONCLUSION

Shift of the spectrum along the wavelength axis is not observed for coatings formed from powder materials. Hypochromic effect causes a shift in color tone largely for achromatic materials. The necessity of using a system of equations taking all account the concentration of pigments in the powder materials was determined. ♦

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NEWS

A NEW BRIDGE OVER THE RIVER TOBOL: TRANSPORT INFRASTRUCTURE DEVELOPMENT AND ENVIRONMENTAL SAFETY

At the end of 2014, a bridge on the river Tobol, along the Tyumen–Yalutorovsk–Ishim–Omsk federal highway in the



Tyumen Area was opened to support smooth movement of vehicles and improved road safety.

The previous bridge at this site was built in 1978, and its traffic capacity has become absolutely inadequate. The new bridge complies with demanding environmental standards.

Igor Kholmanskikh, Authorized Representative of Russia's President in the Ural Federal District, Vladimir Yakushev, Governor of the Tyumen Area, Nikolay Russu, CEO of Mostostroy 11 OJSC, and other dignitaries attended the inauguration ceremony.

VMP Holding, a Russian manufacturer of protective materials with facilities in the Ural Federal District and the North-Western Federal District, participated in the project. Corrosion protection for bridge metalwork was provided with the VMP materials: VINICOR-061 + VINICOR-62. The coating based on these materials is resistant to oil, petrol and corrosive media. It may be applied on surfaces with residual rust or used in paint jobs at subzero temperatures.

EFFECT OF MOLECULAR STRUCTURE OF EPOXY OLIGOMERS WITH PERFLUORINATED FRAGMENTS ON HYDROPHOBIC PROPERTIES OF POWDER COATINGS

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Coatings based on epoxy film-forming agents are used in many industries such as shipbuilding, construction, engineering, etc. Chemical resistance, water resistance, heat resistance, strength, durability are their main advantages.

Corrosion resistance of epoxy coatings is due largely to their high adhesion to various substrates because of the presence of polar hydroxyl groups in the structure of epoxy oligomer. However, the presence of polar hydroxyl groups increases the hydrophilicity of the coating, the propensity to sorption of water and corrosive agents and, consequently, reduces its protective properties.

The following approaches aimed at reducing the kinetic parameters of the diffusion of corrosive agents in the coating are used as conventional methods of an increase in corrosion resistance: compaction of physical and chemical networks, the introduction of fillers (nanoparticles of various morphologies, anticorrosive pigments, etc.). At the same time, little attention is paid to the polarity of polymer coatings, which can make a significant contribution to the diffusion of corrosive agents. Using the non-polar hydrophobic polymers (fluoropolymers, silicones) allows creation of a thermodynamic barrier to the ingress of water and corrosive agents, however, such coatings have low adhesion.

At the same time, the possibility to combine the properties of polar and nonpolar materials occurs and it is implemented in so-called gradient coatings, in which the properties of the polymer matrix can be selectively varied along the thickness of the coating from the substrate to the surface: from polar to non-polar.

A method based on introduction of various waterproof additives in the paint compositions is considered as most technologically and environmentally prospective for creation of gradient coatings. Advantages of this method are discussed in detail in [1–3]. The concept itself consists in migration of hydrophobic additive to the near-surface layers of the coating in the course of film formation and the formation of a non-polar surface with keeping other physical and mechanical parameters of the coating. Among such additives those that are the most efficient and include fluorine-containing fragments attract great attention. Therewith the majority of researches relates to liquid paint materials and data on modifications of powder epoxy compositions and coatings with such additives are limited.

It should also be noted that there are currently no clear ideas about the mechanism of the formation of gradient fluorine-containing polymer coatings, which make it possible to formulate the specific requirements for chemical composition and structure of waterproof additives and their dependence on the nature of film-forming agents, preparation conditions of composite materials and the forma-



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tion of coatings, and other factors allowing to achieve maximum efficiency in the case of using the modifiers.

The aim of the study is investigation of the influence of the chemical structure of some of the synthesized epoxy oligomers containing various amounts of perfluorinated fragments on their efficiency in reducing the surface energy of the coatings produced from powder epoxy compositions.

EXPERIMENTAL

Synthesized epoxy oligomers containing different number of perfluorinated fragments C_8F_{17} obtained by substitution of one, two or five hydroxyl groups in the molecule structure of the epoxy oligomer were used as objects of study. The starting materials for the synthesis: epoxy oligomer of a grade DER 664 (Dow Chemical Company, Germany) with a molecular weight $M_n = 1800 \text{ g mol}^{-1}$, the content of epoxy groups of 4.7 wt %, softening temperature 110°C ; perfluoropelargonic acid chloride (99.5%, Sigma-Aldrich, Germany), bp = 160°C ; N-methylmorpholine (MM) (99.0% Vekton, RF), bp = $115\text{--}116^\circ\text{C}$, $n_D^{20} 1.435$; tetrahydrofuran (THF) used as the solvent (99.0% Vekton, RF), bp = 66°C , $n_D^{20} 1.407$.

N-methylmorpholine and tetrahydrofuran were preliminarily kept over KOH for three days and distilled at atmospheric pressure immediately before the synthesis. Other reagents were used without additional purification.

Synthesis was carried out in one step in tetrahydrofuran medium at a 20 wt % concentration of reactants according to Scheme 1.

Replacement of one, two or all hydroxyl groups of the epoxy oligomer were achieved by varying the ratio of reactants. Stoichiometric amounts of precursors were used in the case of modifiers with one and two substituted groups. Perfluoropelargonic acid chloride was taken in a 30% molar excess relative to the stoichiometric quantity to achieve the complete replacement of the hydroxyl groups in the epoxy oligomer. Product yield after isolation and purification was 80–88% of the theoretically possible. The composition and structure

of the synthesized compounds was established by spectral methods (^1H NMR, IR) and chemical analysis.

^1H NMR spectra were recorded in deuterated trichloromethane solution (CDCl_3) of concentration of 7.10% on an instrument Bruker SW400 (400 MHz). Tetramethylsilane was used as the internal standard. IR spectra of the test substances were obtained on a Shimadzu FTIR-8400S in KBr. Epoxy number was determined by chemical analysis in accordance with the methods described in [4]. The softening point of the products obtained was determined by ring and ball method [5].

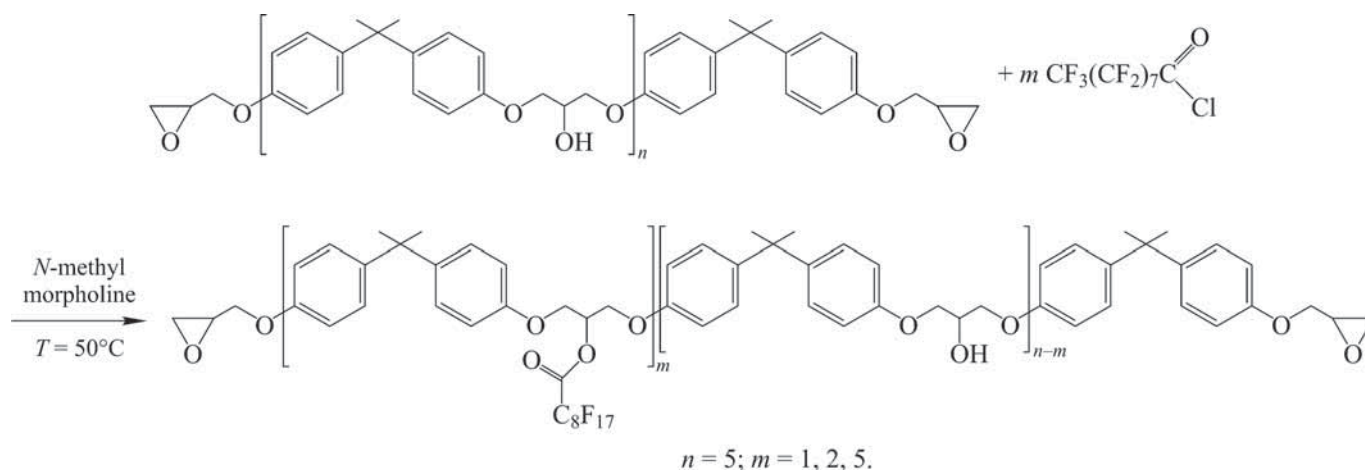
A typical synthesis was described by the preparation of the epoxy oligomer with a perfluorinated radical in the molecule (product EOF1).

The synthesis was performed in the four-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and dropping funnel.

A solution of 16.73 g (8.920 mmol) of DER 664 and 0.92 g (8.920 mmol) of N-methylmorpholine in 70.59 g of tetrahydrofuran was charged to the flask at room temperature and a continuous stream of argon. Then, a solution of 4.36 g (8.920 mmol) of perfluoropelargonic acid chloride in 17.42 g of THF was added slowly ($\sim 60 \text{ min}$) dropwise to the flask at constant stirring.

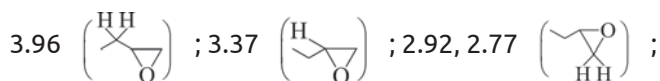
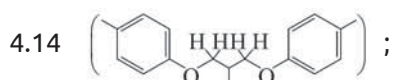
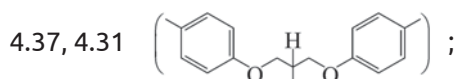
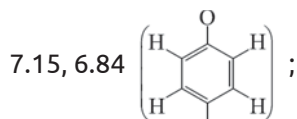
After finishing the dropping the reaction mixture temperature was raised to $50\text{--}55^\circ\text{C}$ and kept at this temperature for 5 h. Reaction monitoring was carried out by IR spectroscopy till reaching a constant intensity value of the absorption band in the 3424 cm^{-1} corresponding to the stretching vibrations of OH-group. For separating the reaction product the reaction mixture precooled to 20°C was slowly added to a 10-fold volume of distilled water. The precipitate was separated by filtration on a Buchner funnel and then dried in vacuo at a residual pressure of 2.1 mmHg to constant weight over phosphorus pentoxide.

The resulting product EOF1: The white solid, soluble in chloroform, N,N-dimethylformamide, tetrahydrofuran, insoluble in water, ethanol, pentane, toluene. The yield of product was 88% of theory. The IR spec-



Scheme 1.

trum, ν , cm^{-1} : 3424, 3036, 2964, 2931, 2874, 1786, 1686, 1607, 1582, 1510, 1460, 1414, 1384, 1364, 1298, 1242, 1182, 1150, 1108, 1084, 1038, 1011, 949, 900, 828, 729, 671, 556. ^1H NMR spectrum, δ , ppm:

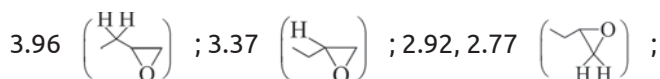
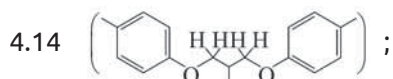
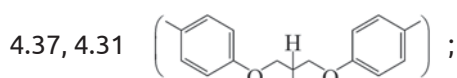
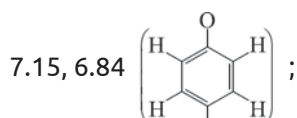


4.37 (-OH); 1.66 (-CH₃).

Modifiers with two (EOF2) and five (EOF5) substituted OH groups were synthesized as described.

The resulting products EOF2 and EOF5 are white solids, soluble in chloroform, N,N-dimethylformamide, tetrahydrofuran, insoluble in water, ethanol, pentane, toluene. The product yield was 84 and 80%, respectively.

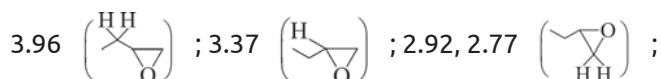
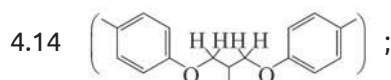
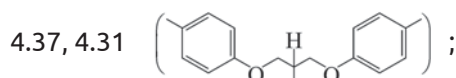
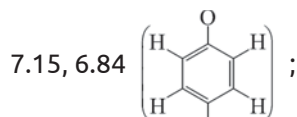
Modifier EOF2. The IR spectrum, ν , cm^{-1} : 3421, 3036, 2967, 2936, 2874, 1784, 1684, 1607, 1582, 1510, 1460, 1412, 1384, 1363, 1298, 1237, 1184, 1149, 1109, 1085, 1040, 1011, 956, 895, 829, 723, 671, 639, 557. ^1H NMR spectrum, δ , ppm:



4.37 (-OH); 1.66 (-CH₃).

Modifier EOF5. The IR spectrum, ν , cm^{-1} : 3038, 2970, 2937, 2876, 1785, 1686, 1608, 1584, 1511, 1461, 1411, 1384, 1364, 1298, 1239, 1217, 1184, 1148, 1117, 1040, 1011, 987, 877, 830, 777, 723, 671, 650, 558.

^1H NMR spectrum, δ , ppm:



4.37 (-OH); 1.66 (-CH₃).

Parameters of the resulting products are listed in Table 1.

The synthesized products were used as modifiers in preparing the compositions and coatings based on solid epoxy oligomer of company Dow Chemical Company, Germany. Modifier content in the powder composition was varied from 0 to 2.0 wt %.

Compositions were prepared by pre-mixing the epoxy oligomer DER 664, fluorine-containing modifier, hardener Casamid 780 (Thomas Swen & Co Ltd, England), and pouring regulator BYK 366 (BYK Chemie, Germany). The components were ground in a ball mill for 4 h at avalanche-like falling of counterbodies followed by homogenization in the melt at a temperature of 125–130 °C. The resulting melt is cooled, crushed, milled, and sieved through a sieve with a mesh size of 125 μm . Coatings were prepared by applying in electrostatic field in the corona discharge at 50 kV to previously cleaned and prepared steel plates of thickness of 0.8 mm. Curing of the coatings were conducted at 180 °C for 20 min. Tests of the coatings produced on impact strength were performed on a device U-1 in accordance with State Standard GOST 53007-2008 (ISO 6272-1:2002 and ISO 6272-2:2002). Degree of cure was determined by a content of gel fraction [6]. Adhesion was determined according to GOST 15140-78 (Method 1 and Method 2) and GOST R 52740-2007 (ISO 15159:2002).

Surface properties of the coatings were evaluated based on the effective boundary water and cetane contact angles [1]. The extended model of Fowke also known as the OWRK theory (Owens–Wendt–Rebel–Kaelble) describing the dependence of the total surface energy of contact angles of polar and nonpolar liquids was used for calculation of the surface energy (SE):

$$\gamma_l (1 + \cos\theta) = 2\sqrt{\gamma_s^d \gamma_l^d} - 2\sqrt{\gamma_s^p \gamma_l^p},$$

where γ_l^d , γ_l^p , γ_l is dispersion, polar, and total surface energy of the wetting liquid, respectively (mJ m^{-2}); γ_s^d , γ_s^p , γ_s is dispersion, polar, and total surface energy of polymer–air surface, respectively (mJ m^{-2}).

Table 1. Characteristics of fluorine-containing modifiers

Modifier	Molecular weight, g mol ⁻¹		Number of groups		Epoxy group content, wt %	T _{soft} , °C
	calculation	experiment ^a	-C ₈ F ₁₇	-OH		
EOF1	2247	2246	1	4	3.8	86
EOF2	2694	2622	2	3	3.3	68
EOF5	4035	3996	5	0	2.2	52

^aThe molecular weight of the synthesized compounds were determined by the value of epoxy numbers.

RESULTS AND DISCUSSION

Often the comparison of modifiers relative to their mass content in composites does not allow correct assessment of their efficiency. Therefore, comparison of the efficiency of synthesized fluorinated oligomers EOF1, EOF2, and EOF5 was performed relative to a weight concentration of fluorine in the coating. Figure 1 shows graphs of the contact angles of coatings on the fluorine concentration.

It can be seen that upon an increase in the fluorine concentration in coatings their hydro- and oleophobic properties increase. Thus, when the fluorine concentration of 0.2 wt %, water contact angle increase from 72° to 85–92°, cetane contact angle θ , from 5° to 23–36°

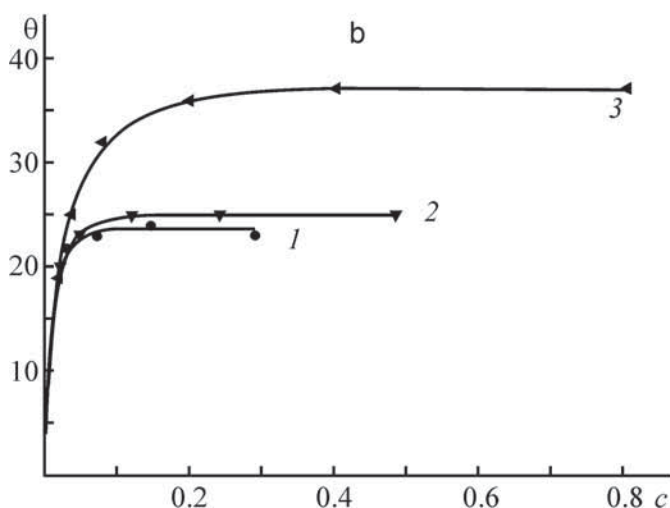
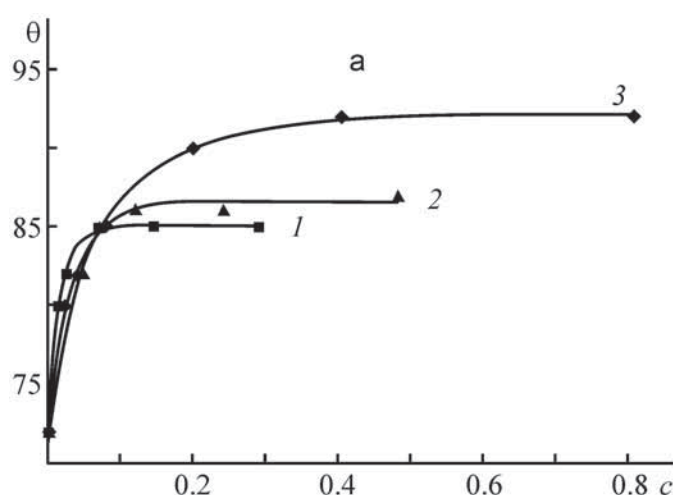


Fig. 1. Effect of fluorine concentration c (wt %) on the effective contact angle θ (deg) of coatings with (a) water and (b) cetane. Modifier: (1) EOF1, (2) EOF2, (3) EOF5; the same for Figs. 2, 3

°. Therewith the efficiency of modifier EOF5 at the same fluorine content in the coating is much higher than that of modifiers EOF1 and EOF2. Presumably, this may be due not only to differences in compatibility of modifiers with an epoxy oligomer, but to different content of side perfluoroalkyl fragments along an oligomer chain. In the case of EOF5 after replacement of all the hydroxyl groups the blocks of perfluoroalkyl fragments -C₈F₁₇ in the side branches are formed, which enter the structure of a polymeric matrix in the process of curing. As shown in several studies [7, 8], in the process of film formation such structures are capable of self-organization on the surface to form a highly ordered perfluoroalkyl chains until crystallization that provides the greatest enrichment of the surface by fluorine-containing clusters.

For a more detailed analysis of the results the dependence of the contact angle on the molar concentration of the modifiers was constructed (Fig. 2).

It is seen that the modifier EOF5 with the highest number of perfluoroalkyl fragments in the molecule exhibits the greatest efficiency that is reflected in the growth of the initial slope of the curves and the values of the angle θ on the saturation line.

Different growth dynamics of the contact angles at low concentrations (≤ 0.5 mol %), apparently, is due to the difference in the driving force of Gibbs adsorption process owing to the different surface activity of modifiers under study. The difference in the values of contact angles on the saturation line, *ceteris paribus*, is likely an evidence of different concentrations of

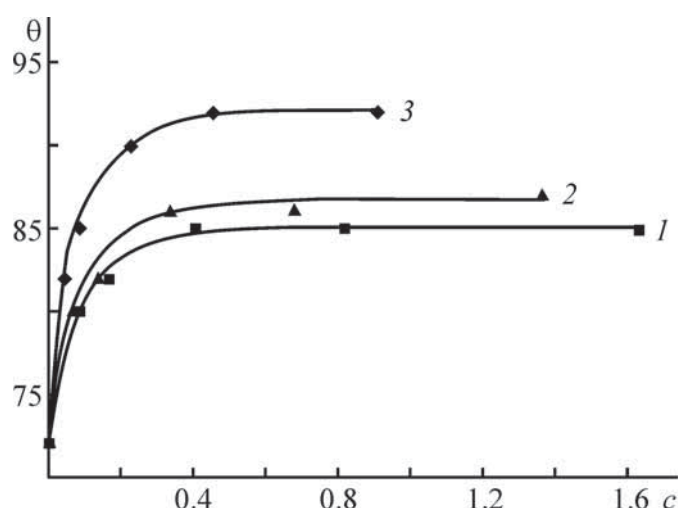
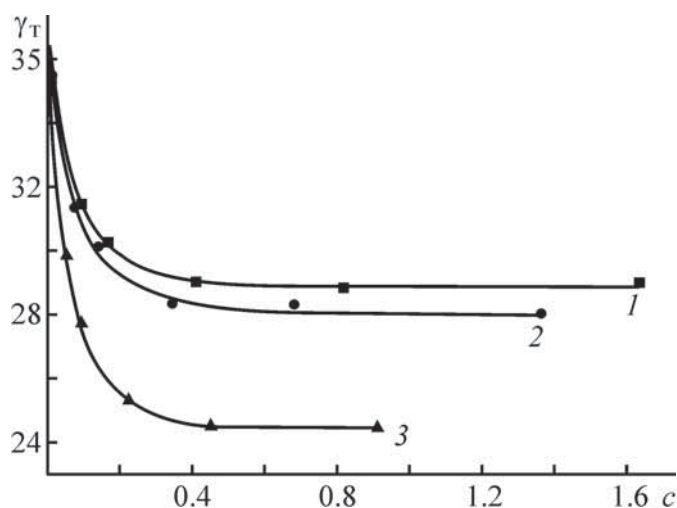


Fig. 2. Effect of molar concentration of modifiers c (mol %) on the effective contact angle θ (deg) of coatings with water

Table 2. Surface energy of coatings with different contents of modifiers

Modifier content			Surface energy, mJ m ⁻²		
wt %	wt % of fluorine	mol %	γ_s^d	γ_s^p	γ_s
No modifier					
0	0	0	8.8	27.5	36.3
Modifier EOF1					
0.10	0.015	0.08	5.3	26.1	31.4
0.25	0.029	0.16	4.6	25.6	30.2
0.50	0.073	0.41	3.5	25.5	29.0
1.00	0.146	0.82	3.6	25.3	28.9
2.00	0.293	1.64	3.5	25.5	29.0
Modifier EOF2					
0.10	0.024	0.07	5.3	26.0	31.3
0.25	0.049	0.14	4.6	25.5	30.1
0.50	0.122	0.34	3.3	25.1	28.4
1.00	0.243	0.68	3.3	25.1	28.4
2.00	0.487	1.37	2.9	25.1	28.0
Modifier EOF5					
0.10	0.040	0.05	4.8	25.1	29.9
0.25	0.081	0.09	4.1	23.6	27.7
0.50	0.202	0.23	2.7	22.6	25.3
1.00	0.405	0.45	2.1	22.3	24.4
2.00	0.809	0.91	2.1	22.3	24.4

Fig. 3. Total surface energy coatings γ_s (mJ m⁻²) vs. the molar concentration (mol %) of modifiers

perfluoroalkyl fragments at the polymer–air interface.

The surface energy is complex characteristic of the surface properties of solids. Its dependence on the concentration of the modifier is shown in Fig. 3 and Table 2.

It is seen that the total surface energy reduction occurs due to a decrease in both the dispersion and polar components, but a drastic decrease in the polar component (2–3 times) is a major contributor to low surface energy of fluorine-containing coatings. This indicates an enrichment of the interface by nonpolar perfluoroalkyl fragments.

It should be noted that, melts of solid epoxy oligomers are of a much higher viscosity unlike low-viscosity liquid epoxy composition. This may be a cause of the fact that the coating produced based on powder compositions possess lower hydro- and oleophobic properties due to the slow process of enrichment of the near surface layers of coatings by molecules modifiers [3, 9]. Moreover, unlike the UV-curable powder compositions, in which in the film formation the process of migration of fluorine-containing modifier to the interface coating–air is separated in time from the process of forming three-dimensional network of polymer matrix, while in the investigated system these processes proceed simultaneously and they are competitive. This is shown schematically in Fig. 4.

To eliminate the influence of factors (high viscosity, gelation process) hindering migration of synthesized modifiers to the coating–air interface, uncured coatings were obtained from solutions of epoxy oligomer in chloroform with additives EOF5 at 20 °C without a curing agent on metallic substrates. Data on the hydro- and oleophobic characteristics of coatings obtained are presented in Fig. 5.

It can be seen the removal of the factors limiting the migration of fluorine-containing modifiers can significantly improve the efficiency of the studied additives. For example, for modifier EOF5 at a concentration of 0.2 mol % the values of the water contact angle increase from 87 ° to 101 °, those of cetane contact angle, from 32 ° to 57 °. The data obtained are in good agreement with the results of [9], in which by melt polyurethane

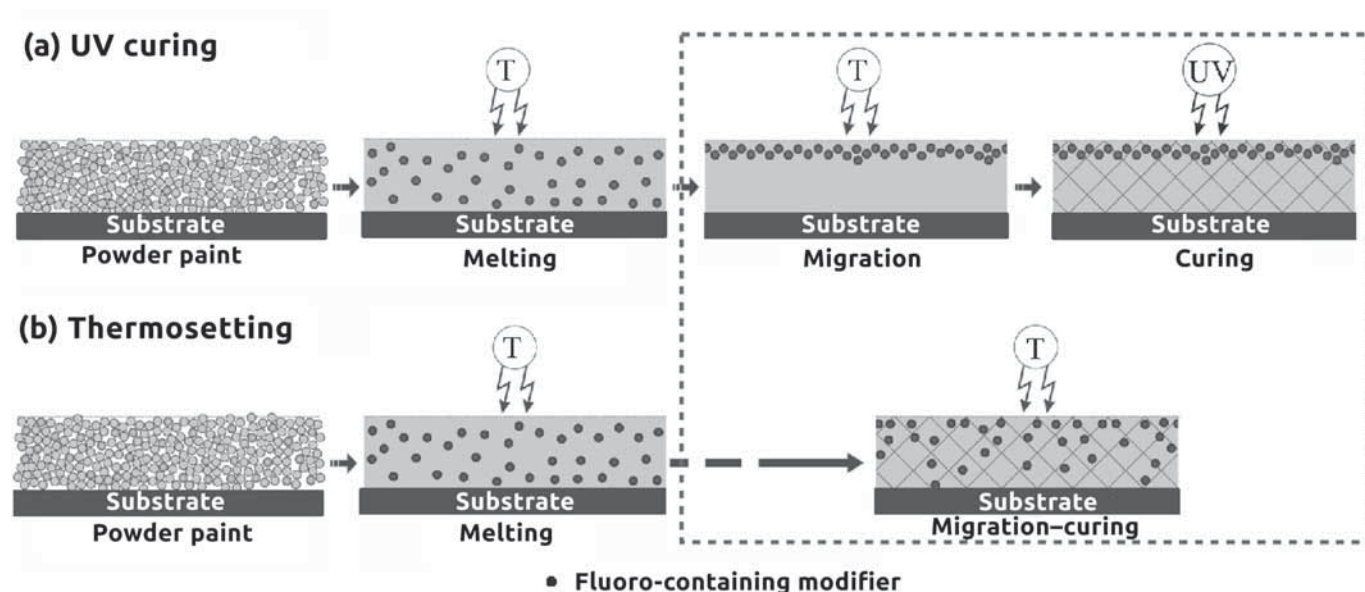


Fig. 4. Scheme of modifier migration upon the formation of coatings from (a) UV curable powder and (b) thermosetting compositions

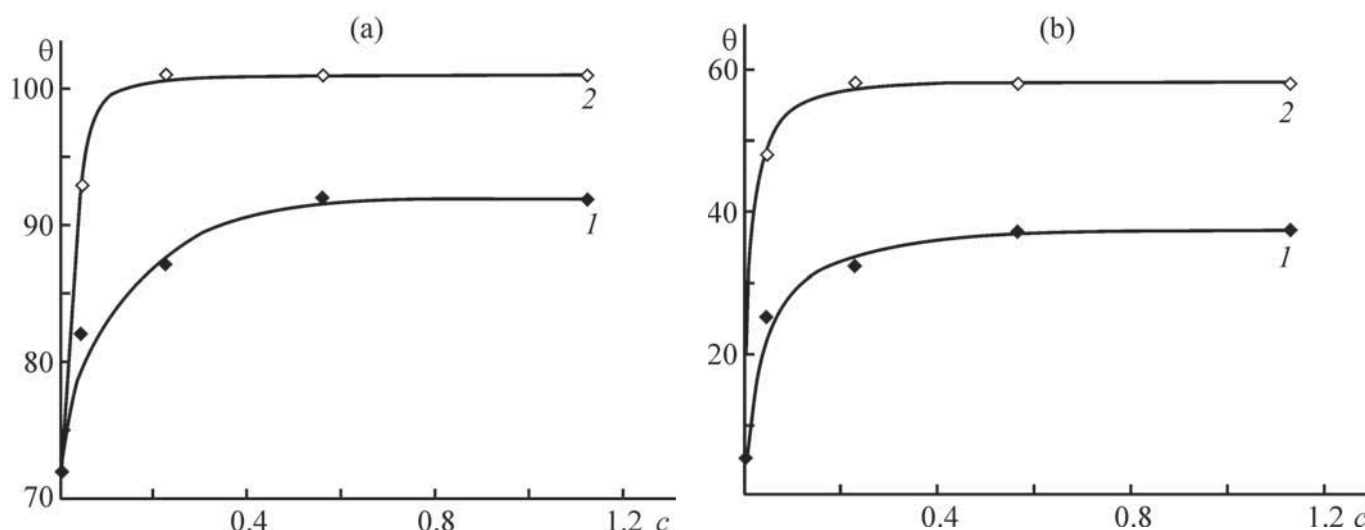


Fig. 5. Effect of molar concentration c (mol %) of modifier EOF5 on effective contact angle θ (deg) of (1) cured and (2) uncured coatings with (a) water and (b) cetane

Table 3. Physical and mechanical properties of the modified coatings

Modifier concentration, wt %	Resistance to shock, cm		Elasticity by Erichsen test, score	Adhesion score	Adhesion strength, N m ⁻¹	Gel-fraction content, %
	direct	inverse				
0.00	100	100	9.0	1	630	92
0.10	100	100	9.0	1	630	93
0.25	100	100	9.0	1	630	92
0.50	100	100	9.0	1	630	93
1.00	100	100	9.0	2	580	93
2.00	100	100	9.0	2	500	93

systems it was shown that a significant decrease in the efficiency of fluorine-containing modifiers proceeds with decreasing the gel formation time.

As it is well known, a significant drawback of fluorine-containing polymers and coatings is their poor adhesion to most substrates. However, the possibility of

formation of coatings gradient by composition in the process of film formation allows balancing the surface and bulk properties of the coatings.

As an example Table 3 shows the physical and mechanical properties of the cured coatings containing various concentrations of EOF5.

It can be seen that in the range of low concentrations of fluorine-containing oligomer (≤ 0.5 wt%) modification of coatings has virtually no effects on their physical and mechanical properties. Only at concentrations of modifier, which significantly exceed the values appropriate for achieving the saturation curve of the contact angle θ on the concentration (Fig. 1), there is some reduction in adhesion strength of coatings. Thus, when the concentration of the modifier EOF5 2.00 wt % (0.81 wt % of fluorine), the adhesive strength of the coating is reduced to 500 N m^{-1} (1.3-fold) that may be due to the presence of the modifier on the interface substrate-polymer owing to its incomplete migration to the interface coating-air.

CONCLUSIONS

(1) Synthesis of a series of new epoxy oligomers with perfluorinated fragments- C_8F_{17} was developed and implemented by reaction of epoxy oligomer with perfluoropelargonic acid chloride in tetrahydrofuran solution. Their composition and structure were established by ^1H NMR, IR spectroscopy and chemical analysis.

(2) It was found that the synthesized products can be used as modifiers for epoxy powder composition for production of coatings with improved hydrophobic properties. EOF5 modifier containing five perfluorinated radicals C_8F_{17} is of the most efficiency. At its content in the compositions of 0.4 wt % of fluorine the contact angle of the coating is 92° .

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NEWS

EMPILS: 2014-2015 RESULTS AND PLANS

In 2014, consolidated sales of the Empils CJSC products (paints for construction and decorative applications, semi-finished varnishes for enamel manufacture, industrial coatings) exceeded those in 2013 by 7% in monetary terms, and by 4% in volume.

Empils leads the domestic production of alkyd coatings: upon increasing its output of solvent-borne paints by 12% compared to 2013, the company ranked first according to the ratings of Russia's major paint manufacturers compiled by Chem-Courier analytic agency. Also, based on the 2014 results, Empils CJSC ranks in the top 10 of water-based coatings manufacturers.

In the previous year, sales of industrial coatings and semi-finished varnish used in the manufacture of alkyd enamels have increased significantly: according to the company, the growth was 58% in monetary terms (60% in tons).

In the course of the year, Empils continued to develop product portfolio in the DIY segment: water-dispersion products under the Newtone brand name were introduced to the market, new products in the Profiwood range of wood coatings were developed and made commercially available, along with the Titan coatings for metals.

The company's optimistic scenario for 2015 envisages sales growth by 15% (in monetary terms). Priority areas include segments of water-based coatings, specialised coatings, semi-finished varnishes, and industrial coatings.

In the course of the year, the company intends to continue development and introduction to the market of new products, further develop its distribution system across all regions of Russia and CIS countries, as well as to pursue activities focused on higher manufacturing efficiency. Empils CJSC is currently implementing a programme of upgrading its production facilities, including the construction of a new varnish plant. The company's advanced technological complex will enable the manufacture of entirely new products, mostly in the segment of industrial coatings.



ADHESION OF ICE TO POWDER COATINGS SURFACE

Dr. A. Ilinykh, Prof. A. Yakovlev, ECOLON PC JSC; **Dr. I. Korolev, A. Orlov**, Ftorkraska Ltd., Russia, St. Petersburg

Special purpose powder coatings for targeted use, that can replace conventional liquid and mainly solvent-borne coatings, get more and more attention as the production of powder coatings grows. Anti-icing compositions and coatings can become one of the most demanded among these special purpose materials.

In the course of exploitation coating interacts both with the substrate and with the environment — be it gaseous or liquid and often with solid substances of varied chemical composition. In interaction with the substrate usually the maximum adhesion is wanted, in the interaction with the outer substances — the minimal possible. Solid substances that most commonly come in contact with coated surface are ice, frozen soils, paraffin residue from oil, dried baking dough.

Anti-icing coatings get the most limelight in the professional literature [1–5]. The demand for such coatings comes both from production and from construction. Industries that engage vessels, aircraft, hydrotechnical constructions, power engines and other land facilities, have a great need for anti-icing solutions. Low-adhesion coatings with anti-icing properties are useful in food industry as well, at storage and transportation of frozen foods.

In present days the problems of icing and combating icy caps buildup are in the spotlight due to the vast development of offshore oil and gas in the Arctic region. Icing up of power lines is also a big problem. In the last 50 years much work was done to find the solution to this and various ways of prevention ice build-up and diminishing the strength of its adhesion to surfaces were offered [6,7].

The most radical method for combating ice build-up is the chemical method, namely treating the surface with antifreeze substances, that put the freezing point in very low temperature range. Various soluble substances, both solid and liquid, of organic and inorganic origin, can serve as antifreeze. Salt based antifreezes that provide the lowest freezing points contain alkaline and alkaline-earth metals chlorides, organic antifreezes are usually based on glycols, spirits and amines. The freezing point of the mixture of 32% CaCl_2 , 7% NaCl and 61% water is -45°C .

Despite the wide use of antifreeze in car engines cooling systems, in anti-icing treatment of aircraft, runways, city streets, their use in treating ships and hydraulic structures is restricted due to complexity of reliable application and to washing-off. Coatings containing antifreeze turned out to be ineffective because of hydrophilicity, low water resistance and limited protection time [1]. In addition, salts in antifreezes are strong activators of metal corrosion.

Coatings with low surface energy and good slip properties are used for protection of vessels and hydraulic constructions from icing. Such coatings do not prevent ice formation on the surface but let ice be removed more easily [4]. Connection between surface characteristics and ice adhesion to it is known for long. The crucial factors are: the degree of hydrophilicity (or hydrophobicity) of the surface, its force field, thermophysical characteristics, structure, degree of roughness [6].

Condition and quality of water has also been taken into account — its chemical composition, temperature and freezing conditions. Studies shown that freezing at -30°C increased the adhesion of ice to the surface by 20–40% compared to freezing at 0°C [6]. Increase of the water salinity reduces adhesion of ice in impressive 3–5 times compared to distilled water.

In the ice formation process there is a liquid phase, which is why most theoretical pre-suppositions in developing anti-icing compositions are based on the theory of surface interactions (solid–liquid–gas) on the interphase boundary according to Young's equation:



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$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv} \times \cos\theta,$$

where θ is the contact angle.

In the process of water turning into ice surface tension grows from 72 mJ/m² (for water) to 120 mJ/m² (for ice). With the increase of surface energy grows the work of adhesion W_A , which is the ratio of the work W_s spent on pulling-off adherent substance (water, ice) from the substrate (S) [8].

The adhesive force of ice (adhesion strength) to most substrates (especially of hydrophilic kind such as metals, glass, concrete, wood) is quite high and reaches hundreds of kPa. Adhesion of ice exceeds its cohesion. In case of coatings as substrate, adhesion of ice drops drastically with increasing surface hydrophobicity. So, on epoxy coatings (surface energy $\gamma = 44$ mJ/m², wetting angle $\theta = 56$ degrees) adhesion strength of ice (A) equals 52 kPa. At coatings based on polytetrafluorethylene (PTFE) ($\gamma = 22$ mJ/m², $\theta = 94$ degrees) $A = 15$ kPa¹[6].

Not coincidentally, in developing the formulation for anti-ice coating researchers focus on hydrophobic and superhydrophobic coatings with θ equalling 120–150 degrees. [7, 9–10]. Such coatings are badly wetted with water, so the adhesion of ice to them, as a rule, does not exceed 10–15 kPa. Obstacle to the wide application of these coatings is the instability of their hydrophobic properties. Hydrophobicity deteriorates with time under the influence of the environment [11]. So, the problem of developing stable anti-ice coating is not yet solved.

In this work we present you the results of the attempt to formulate powder coatings with low adhesion to ice.

The objects of study were non-pigmented powder coatings based on epoxy, polyester and polyurethane resins with different types of modifiers. Epoxy powder compositions are based on novolac epoxy oligomer of the 4th type (epoxy equivalent weight 500–560, softening point 89–97 °C) and low molecular weight 3-type epoxy resin (epoxy equivalent weight 740–800, softening point 98–104 °C).

Polyester powder compositions are based on carboxyl terminated polyesters (acid number 30–38 mg KOH/g, glass transition temperature: 67 °C). As hardeners we use triglycidil isocyanurate (TGIC) and β -hydroxyalkylamid.

Polyurethane compositions are based on hydroxyl-terminated polyester resin (hydroxyl number 26–34 mg KOH/g of glass transition temperature of about 60 °C) and hardener — caprolactam-blocked polyisocyanate (NCO content 15,3%), as well as the dibutyltine oxide curing catalyst.

Polyacrylate modifiers, fluoropolyols, as well as silicone oligomers with hydroxyl groups (contents of the OH groups — 6%, glass transition temperature 41–47 °C) and silicone copolymers with different structures were used to control flow and surface properties. Benzoin was used to de-gas the compositions.

Powder coatings were produced by standard technology: premixing of components in a ball mill for 1 hour, extrusion in laboratory twinscrew extruder at

100 °C, grinding the centrifugal mill, sieving through the sieve 0100.

Coatings then were applied on the degreased cylinder weights and plates by spraying in electrostatic field at voltage on discharge electrode of 40 kV and cured in the oven at 180 °C for 20 minutes.

Adhesion force was measured as the coated cylinder weights were pulled off the icy surface at the Posi Test AT-M device by De Felsko (USA) (Fig. 1), in accordance with ISO 4624 (method 2) using cylinder weight with a diameter of 20 mm. The test procedure was the following: first we frosted a block of ice at least 5 cm high in the fridge at –18 °C for 3 hours. Then put the coated weight on the surface and kept for two more hours at the same temperature. The trim of the frozen cylinder was treated with the special instrument to eliminate the trim effects. Then the manual drive was attached to the cylinder weight and pulled the cylinder off at speed not exceeding 1 MPa/s. The test device registers the value in MPa at the moment of the pull-off. The cylinders were frozen for at least 10 cycles during the test. We took into consideration only the measurements at the adhesive pull-off. Measurements of the cohesion pull-off were discarded.



Fig.1. Posi Test AT-M

Hydrophobic and oleophobic properties of the coatings were determined by the value of the static wetting angle at wetting by distilled water and *n*-hexadecane according to the traditional methods [12] followed by the calculation of free surface energies of coatings according to the extended Fowks equation:

$$\gamma_{\text{ж}} \times (1 + \cos\theta) = 2 \times \sqrt{\gamma_s^d \times \gamma_l^d} - 2 \times \sqrt{\gamma_s^p \times \gamma_l^p},$$

$$\gamma_s = \gamma_s^d + \gamma_s^p,$$

where $\gamma_l^d, \gamma_l^p, \gamma_l$ is dispersive, polar and total surface energy of wetting liquid respectively, mJ/m²; $\gamma_s^d, \gamma_s^p, \gamma_s$ — dispersive, polar and total surface energy of the polymer surface, respectively, mJ/m².

Table 1 lists the values for different coatings, as well as for aluminum of which the test cylinders are made.

From table 1 we see that the total surface energy of the studied powder coatings is approximately at the same level of 30–35 mJ/m², which is slightly less than that of aluminum. Also close the values of contact angle for water (73–77 degrees) and *n*-hexane (5–10 degrees).

¹The difference in absolute values of the adhesion strength is associated with different methods of measurement.

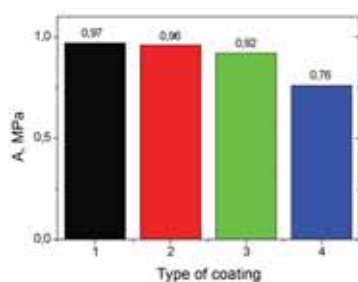


Fig. 2. Adhesion of ice to varied surfaces (1 — aluminum surface without coatings, 2 — polyester, 3 — polyurethane, 4 — epoxy). Coatings are not modified

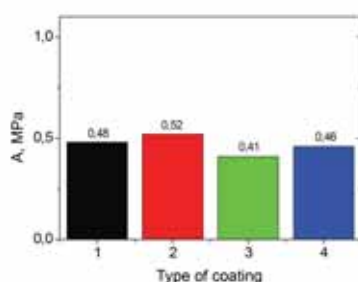


Fig. 3. Adhesion of ice to epoxy coatings with different hardeners: 1 — substituted DICY; 2 — phenolic hardener; 3 — mono-salt of the aromatic polycarboxylic acid and cyclic amidine; 4 — novolac type of epoxy resin, cured with phenolic hardener

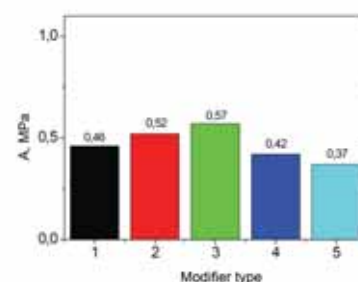


Fig. 4. Effect of modifiers on the adhesion of ice to the epoxy coating. Modifiers: 1 — acrylate; 2 — silicone oligomer; 3 — silicone copolymer; 4 — fluoropoliol; 5 — fluoropoliol 2

Table 1. Contact wetting angles and energy characteristics of the surfaces of different powder coatings

Coating	θ , deg		Energy characteristics of coatings, mJ/m ²		
	Water	n-hexa de-cane	γ_m^d	γ_m^p	γ_m
Polyester	77	10	27.2	6.2	33.4
Polyurethane	78	5	27.5	5.6	33.1
Epoxy	77	5	27.5	6.1	33.6
No coat (Aluminum)	60	5	27.5	14.5	42.0

Determination of the adhesion to the studied coatings has shown that it is varied (Fig. 2). As expected, the adhesion of ice to polymeric coatings is lower than to the uncoated metal (aluminium). Among coatings epoxy powder coatings stand off — adhesion of ice to them is 20–25% lower than to polyester and polyurethane powder coatings.

Noteworthy is that there is no correlation between adhesion of ice to coatings and contact angles. Apparently, wetting angles are not significant indicator of ice adhesion to coatings. Perhaps, the density of crosslinking of polymer molecular chains and their glass transition temperature have more influence on ice adhesion.

It was curious to study the influence of the nature of the hardener on ice adhesion on the sample of epoxy resins. With this coating we used as hardeners: linear phenolic hardener with terminal hydroxyl groups, catalyzed by a imidazoline derivatives; substituted DICY; mono-salt of a aromatic polycarboxylic acid and a cyclic amidine. They were taken in optimal quantities for curing oligomer. Coatings were baked at 180 °C for 20 minutes. The gel-fraction in all samples was close to 100%.

Figure 3 shows the values of the force of adhesion of ice to the studied samples

The test results show that the hardener in powder formulations plays not the least important role in interaction with ice. It is possible that the reason for the differences is the glass transition temperatures of coatings. Water contact angle is approximately at the same level with all the samples and is 79–80 °C. The lowest values occur in epoxy low-molecular weight resin cured by mono-salt of an aromatic polycarboxylic acid and cyclic amidine.

It is known [4–6, 8–9] that one of the ways to reduce the adhesion of ice to coating is the introduction of hydrophobic components, including fluorinated compounds, polyolefins, waxes, siloxanes. In this study this option also was tested. In the formulation of powder epoxy compositions were introduced various hydrophobic modifiers: polyacrylate, organopolysiloxane and copolymers, fluoropoliol. Figure 4 shows the values of adhesion force of ice at the modified coatings.

As can be seen from Fig. 4 the greatest effect on reducing ice adhesion is achieved with the application of fluorinated modifiers. Modification of the compositions with fluoropoliols lowers the surface energy of coating and greatly enhance their hydrophobicity (values of θ reach 92–98 degrees). It is known [9] that good slip is possible at the values of the surface energy of 20–22 mJ/m², which we observed in our experiments.

It was curious to register the change of adhesion of ice to coating in the repeated freeze-thaw cycles. At least 10 cycles were performed to measure the adhesion force of ice. It was noted that it stays the same – at the level of 0.37 MPa for novolac epoxy coatings modified by fluoropoliol 2.

The above presented studies allowed us to formulate the composition of epoxy powder coatings with good anti-icing properties. Industrial production of these powder compositions is arranged in JSC «EKOLON PC» (St.-Petersburg).

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INFLUENCE OF PIGMENT PARTICLE SIZE AND SHAPE ON REACTIVITY OF THE UV-CURED COMPOSITION

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Environmental issues in modern world hold one of the leading positions, that is why there is an acute necessity in obtaining eco-friendly coatings not containing conventional harmful solvents. At the same time there is a tendency to make the coating layer thinner preserving its high protective characteristics and decorative properties. The UV-curing pigmented coatings can match these challenges.

In coatings industry pigment characteristics such as particle sizes and shape are connected with the «hiding power» (opacity) notion. The hiding power (GOST 8784-75) means an ability of a pigmented paint layer applied homogeneously to a monochromatic surface to hide the color of the latter, or, in case of applying to a black-white base, to reduce the contrast between black and white squares until the contrast vanishes. The hiding power of pigment is defined as quantity of paint in kilos (counted on the basis of the PVC) divided by the square of the surface covered (kg/m^2). Measured otherwise, as quantity of square meters that can be fully covered with this amount of pigment in paint, measured in m^2/kg or l , is called opacity.

The hiding power of pigments arises due to diffuse reflection (dissipation) and light absorption in the film and depends on the difference of refractive indices of pigments and binder. The bigger is this difference, the higher is the hiding power. Pigments with refractive index within the range 1.6–1.65, i.e. close to the refractive indices of binder, are called transparent pigments. These include fillers. Pigments, which have the refractive index > 1.65 , are called hiding pigments.

The hiding power increases with reduction of particle size (to a certain limit) and with increase of a pigment volume concentration (PVC): the higher the PVC, the better is the hiding power [1, p.83].



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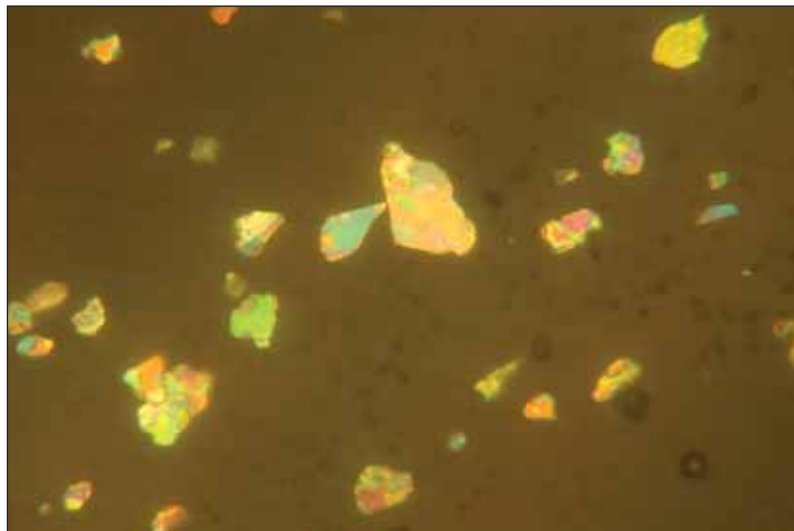


Fig. 1. A pearl pigment particle photo

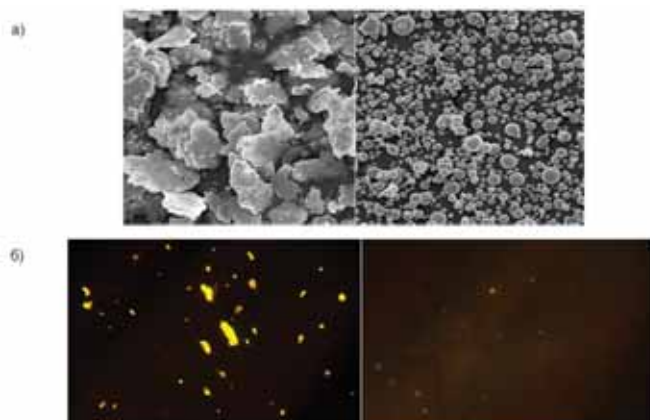


Fig. 2. A photo of pigment particles, introduced to an UV-varnish formulation: a) in a powder; b) in a polymer

Particle sizes influence primarily the color of the pigment. High color saturation is typical for pigments with a lower degree of polydispersity. The color of yellow iron oxide pigments is darker, when the particles are bigger. Pearl pigments, consisting of mica scales with high refractive index, on which metal oxides (mainly TiO_2) of different thicknesses are applied (Picture 1), belong to pigments that create optical effects through interference. The color depends on the thickness of applied layers (40–150 nm) [1, p.85].

Particle shape also influences the optical characteristics of pigments. It can be: a) spherical or cubic (granulated pigments); grainy or needle-shaped (chrome orange); b) platelet of lamellar (mica, metal powders). Photos of the pigment particles of platelet and spherical shape are presented on Fig. 2

Particles of metal fillers of spherical shape are obtained by spraying hot metal in air or water under high pressure.

The lamellar (platelet) pigments have floating or non-floating properties, depending on the substance with which the surface is treated — stearic or oleic acid.

This study is aimed at investigation of the influence of pigment particle size and shape on polymerization rate of UV-curing pigmented compositions.

EXPERIMENTAL

On the basis of epoxy-acrylic varnish «Akrolak-UF» (TU 2316-019-50003914-2006), developed in the NPF INMA, there were prepared three model formulations of UV-cured clear coat (22% of reaction diluent, 12% of photoinitiator mixture, 56% of oligomer) not containing pigments (sample 1), UV-cured clear coat, containing 10% of the pigment of spherical shape (sample 2), and UV clear coat, containing 10% of pigment of flaky shape (sample 3) in a high-speed dissolver through mixing of components of the binder with a photoinitiator during 10 minutes. The clear coat samples were applied on photographic glass plates 9x12 cm in size with wet film thickness of 30 μm . An obtained layer was cured in ORK-21 M1 device with a mercury lamp DRT 400 during 5, 10, 15, 20 and 25 s. Intensity of ultra-violet radiation (H) in

Table 1

No	Carbon grade	Average particle diameter, nm	Specific surface area according to BET, m^2/g
1	Special black 6	17	300
2	Printex U	25	100
3	Special black 100	50	30

UV-A, UV-B, UV-C, UV-V spectrum was registered with an UV-radiometer UV Power Puck II. The intensity of UV-radiation were $\text{HA} = 75 \text{ mW}/\text{cm}^2$; $\text{HB} = 68 \text{ mW}/\text{cm}^2$; $\text{HC} = 12 \text{ mW}/\text{cm}^2$; $\text{HV} = 54 \text{ mW}/\text{cm}^2$. A coating thickness was determined with the «Blade Micrometer MP-25» device (GOST 4381-87). A hiding power of paint was determined in accordance with a visual method (GOST 8784-75). The hardness of the obtained coating with thickness of 25–30 μm was determined with the pendulum TML-2124 (TOR 25-0612.038-86, GOST 5233-89).

With the help of infrared spectrometer Shimadzu FTIR-8400S we defined the IR-spectrum of cured coatings from prepared samples 1, 2, 3 and a non-cured UV-lacquer (sample 4) in a range of wave numbers 400–4000 cm^{-1} , in potassium bromide tablets KBr, obtained by a compaction method.

To study the influence of pigment curing of UV clear coat, different grades of carbon black in content of 1.9% (Table 1) were introduced to its formulation (30% of reaction diluents, 9% of photoinitiator mixture, 59% of oligomer, 0.1% of dispersing medium).

Photos of pigment particles were obtained with a research metallographical microscope MIM-9 (LOMO) with objective $F = 6.3$ without ocular and digital single-lens reflex camera Canon EOS 60D.

DISCUSSION OF RESULTS

The epoxy-acrylic UV-cured clear coat, not containing pigments, has high reactivity, i.e. it is cured almost in seconds up to hardness of 0.30 relative units. With the introduction of a metal pigment of spherical shape to the formulation, the composition reactivity reduces — the cure rate becomes lower, in the presence of flaky

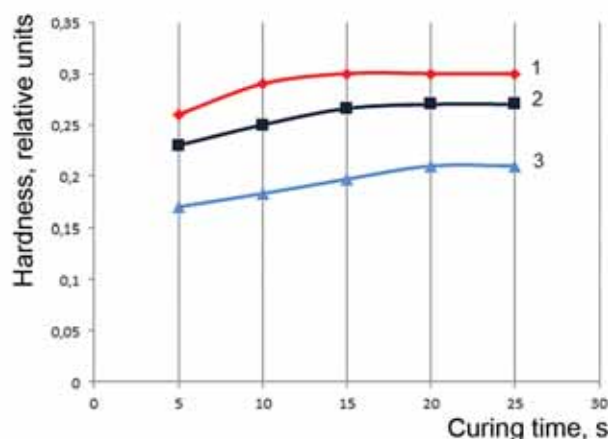


Fig. 3. Dependency diagram of a coating hardness on cure time for samples of: 1 — cured UV clear coat; 2 — UV clear coat + 10% of a spherical pigment; 3 — UV clear coat + 10% of a flaky pigment

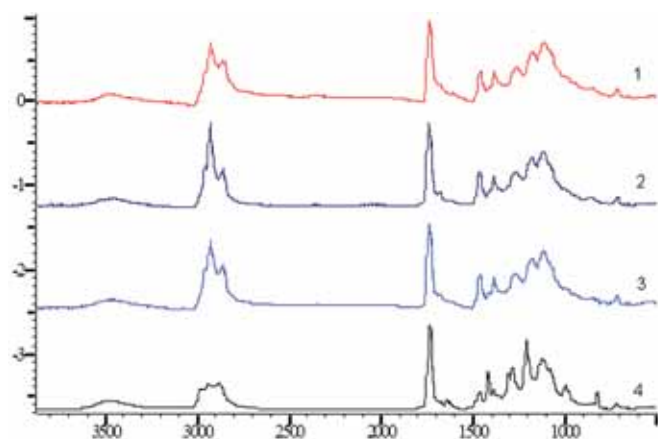


Fig. 4. Sample infrared spectra: 1 — cured UV clear coat; 2 — UV clear coat + 10% of a spherical pigment; 3 — UV clear coat + 10% of a flaky pigment; 4 — non-cured UV clear coat

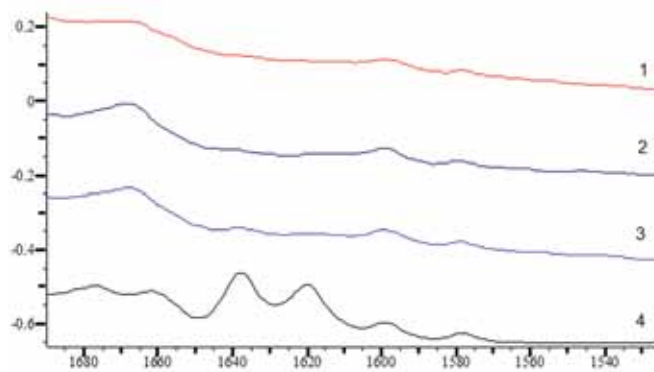


Fig. 5. Stretching vibration bands C=C. Sample infrared spectra: 1 — cured UV clear coat; 2 — UV clear coat + 10% of a spherical pigment; 3 — UV clear coat + 10% of a flaky pigment; 4 — non-cured UV clear coat

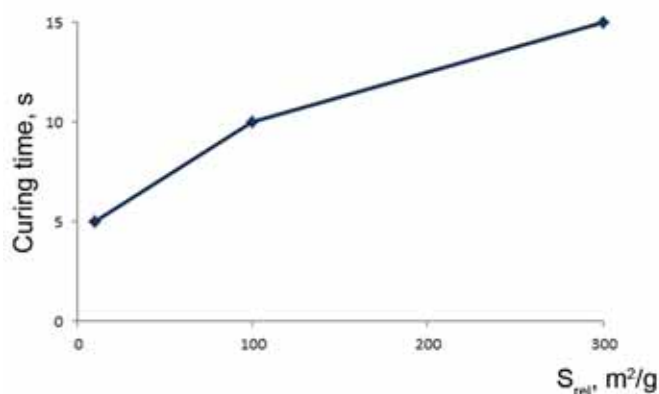


Fig. 6. Dependence of time of cure on a carbon specific surface area

pigments in the UV-lacquer the cure rate reduces greatly (Fig. 3). It is worth noting that visually samples 1 and 2 look like cured after 15 s of UV-radiation, while sample 3 looks liquid (non-cured). The same is proved by a study of infrared spectrum of the samples.

In the spectrum of an initial prepolymer the presence of vinyl bands in spectral regions, typical for them, can be noted. These are bands $3106, 3065$ and 3037 cm^{-1} — of stretching vibration C—H of a vinyl group, and bands $1667, 1662, 1638$ and 1620 cm^{-1} — of stretching vibration C=C (Fig. 4). The presence of several bands can be explained by existence of the vinyl groups in different conformational states of the prepolymer. In cured polymers the indicated bands disappear completely. In sample 3 in comparison with sample 2 the residual bands of the stretch vibration C=C (Fig. 5) are presented.

For coatings pigmented by carbon, with the growth of a specific surface area from 30 to $300\text{ m}^2/\text{g}$ the curing rate goes down (time and dose of cure increase). Depen-

dence of cure time on the specific surface area of carbon is shown in Fig. 6. With the decrease of a pigment particle size, its hiding power increases, therefore, the higher the pigment hiding power is, the slower the cure is.

Pigments in UV-curing compositions cannot be considered as inert additives: they influence not only on decorative and physical and mechanical properties of paint but also the speed and quality of UV-curing. As pigments due to many factors have absorptivity in some regions of the spectrum, their presence in formulations of UV-cured paints, rate and completeness of a polymerization reaction can fall. In the absence of an expert selection of pigments and photoinitiators, they can come in conflict for photons, the result of which can be slowing down or termination of a process of polymerization. Particle sizes and shapes, besides chemical nature, belong to factors affecting the pigment absorption ability.

CONCLUSIONS

1. Pigment particle shape and size influence the curing of pigmented UV-compositions is shown. With reduction of the pigment particle size, the cure rate decreases. When an equal pigment content is in UV-composition formulation, the cure rate of coatings containing spherical pigments is higher than of coatings with flaky ones.

2. It is established that the cure rate depends on a pigment hiding power. ♦

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SURFACE CLEANING OF STEEL OBJECTS WITH DILATANT FLUIDS

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The modern economy suffers from significant losses as the result of corrosion processes, ruining constructions, equipment and works made of iron alloys. Protecting these objects from corrosion is a crucial task, a comprehensive solution of which leads not only to reduction of operating costs, expenses connected with repair and renewal operations and replacement of elements broken down as the result of corrosion damages, but also promotes an increase of engineering safety during exploitation.

The most commonly used way of protection from corrosion today is coating metal surface. Application technology includes the following main stages: surface cleaning from corrosion products, old coatings and other contaminations, that may deteriorate future coatings; degreasing; base coat application and finishing coating application. Consequently, cleaning different surfaces of constructions, elements and works plays a significant role in modern technology, and its quality influences obtained coating performance and its anticorrosive properties directly.

Today the following ways of the surface cleaning are used most commonly: cleaning manually with hummers, scrapers, palette-knives and metal brushes; mechanical cleaning with any power tool, blasting with a jet of dispersed abrasive material, suspension or fluid. It is worth saying that the manual cleaning has the lowest productivity, mechanization of this process increases its productivity greatly, but still the mechanical cleaning can't beat blasting in productivity and effectiveness.

The blast method of cleaning can be divided into: dry blast cleaning, blast cleaning with compressed air, blast cleaning with moisture injection and blast cleaning with fluids under pressure. Most cost effective is the cleaning with the fluid under pressure, but its technical effectiveness is lower than when using traditional blast methods. Indices similar to the blast method effectiveness can be achieved when using pressures more than 100 MPa, that makes the process significantly energy expensive and not safe for an operator.

Implementation of a new working body with anomalous rheological properties, i.e. fluid, having dilatant properties, allows to improve indices of the traditional hydroblastcleaning significantly. It allows to reduce working pressure by times when cleaning and to increase the process effectiveness.

A research team under the guidance of Professor, Doctor of Chem. Sci., Krashennnikov A.I. developed compositions on the basis of waterborne polymers and bentonite, having strongly marked dilatant properties. It means that in increase of shear rate for this fluid, a significant increase of viscosity occurs. At that an interaction with a surface goes to another qualitative level, i.e. the fluid jet interacts with the surface not as fluid, but as a solid body.

Quantitative values for this effect depend on a content of the composition and can be directionally changed in wide ranges for providing the best array of properties.

Microscopic techniques were used for investigation of typical peculiarities of a surface, obtained after hydrocleaning.

Figs 1 and 2 show images of sample surfaces made of constructional steel, undergone scraping (Fig. 1) and blasting with the use of the dilatant working fluid (Fig. 2).

Differences between the mechanically cleaned and hydro-blasted surfaces are shown in the pictures. The mechanically cleaned sample has less developed surface, than the hydro-blasted sample. It allowed us to make an assumption that



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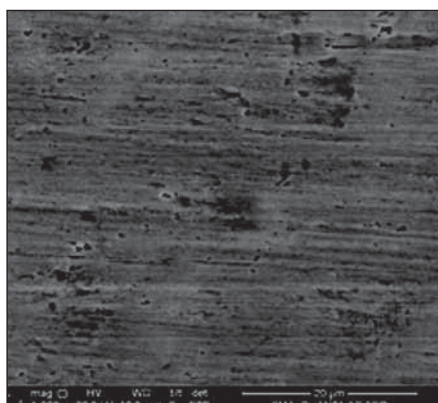


Fig. 1. An image of the scraped sample

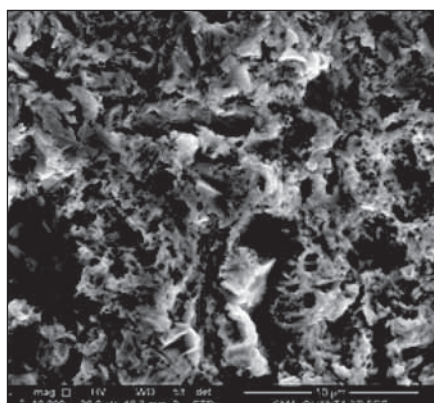


Fig. 2. An image of the hydrocleaned sample

Table 1. Test Results on adhesive strength

Paint material name	Type of cleaning	Paint film thickness, mkm	Nominal toughness before displaying, MPa	Nominal toughness after displaying, MPa	Change of adhesive power during displaying, %	Pull-off type
Gremirust grey	H	340–452	7,26	8,42	14	Cohesive
	M		9,92	7,63	24	
Primprom-korr	H	195–228	2,3	1,52	33	
	M		5,3	3,98	24	
EP-CP	H	172–187	3,6	2,97	17	
	M		3,7	2,87	22	

H – hydrocleaning with dilatant fluids. M – mechanical cleaning

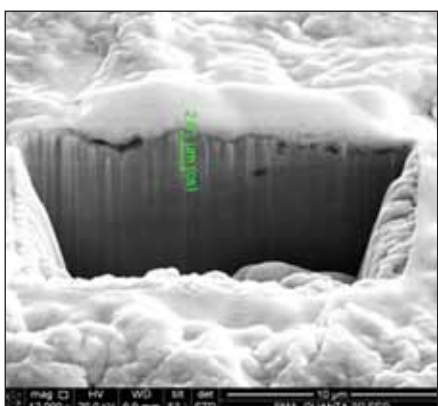


Fig. 3. An image of sample surface coat

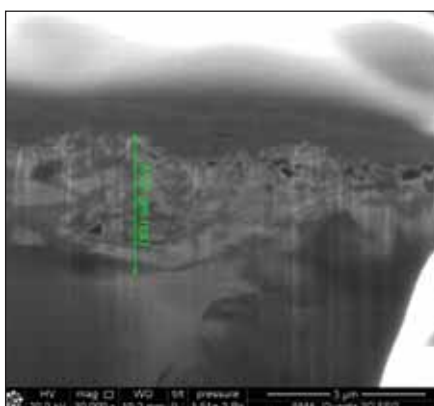


Fig. 4. Cross-section of hydro-blasted sample

coatings, applied on the hydro-blasted metal surface, will have better adhesion indices in comparison with the substrates processed mechanically.

Adhesion tests, performed with a pull-off method according to GOST 27890-88, of samples after 5 month of weather test, confirmed our assumptions. The test results are shown in Table 1.

In the series of tests performed it was established that in several cases the level of adhesive power increased with time.

Figs 3 and 4 show images of surfaces and a cross section of a surface coat of a sample, undergone hydro-blasting.

The given images allowed us to form a clear picture of the properties of the surface, blasted with dilatant fluids, and also of dimensions of the surface coat, the structure and properties of which differ from properties of the original material. The presence of such coat on the surface of the processed material opens an opportunity of usage of the hydro-blasting with dilatant fluids not only for cleaning of surfaces from contaminations but for obtaining surface coats with specific properties.

For revealing the inhibitive effect of polymer film, formed on a metal surface as a result of hydro-blasting, we performed the following studies: tests on weather resistance, impedance studies, and electrochemical investigation.

For determination of weather resistance 3 series of tests were performed:

- 1st series of samples underwent testing according to GOST 9.401-91 «Unified system of corrosion and ageing protection. Coatings. General requirements and methods of accelerated weather tests». In the course of work we used: a wet chamber, providing humidity ($95 \pm 3\%$), and a thermal chamber, in which temperature ($+600 \pm 2^\circ\text{C}$) was maintained automatically.

- 2nd series of samples underwent weather test in natural conditions.

- 3rd series of samples underwent test in artificially created humid environment, imitating atmospheric conditions with 3% solution of NaCl with periodical spraying).

The test shows that samples blasted with dilatant fluid have the same corrosion resistance as mechanically blasted ones.

The impedance studies of systems «base — polymer film of dilatant fluid — coating» were performed in a broadband (100-50000 Hz) at room temperature, 3% solution of NaCl was used as corrosive medium.

In the course of the impedance study it was established that the sample, blasted with dilatant fluid, has better corrosive resistance in 3% solution of NaCl, which is proven through studying of kinetics of change

Table 2. An average value of a weight loss during display in a corrosive medium (NaCl 3%)

Mechanical cleaning	0,006
Cleaning with dilatant fluids	0,0013

of the surface resistance. The conclusion is that a film, formed on a steel surface as a result of dilatant-blasting, has an inhibitive effect.

Also, we performed electrochemical investigations of samples, processed with dilatant fluids, which showed that as the result of the dilatant-blasting a significant metal inhibition occurs, that is confirmed by potentiodynamic studies.

In addition, we performed investigations of corrosion indices and corrosion resistance in accordance with GOST 9.908-85 «Unified system of corrosion and ageing protection. Metals and alloys. Methods for determination of corrosion and corrosion resistance indices». The corrosion indices were determined through an assessment of a weight loss per surface unit area for the samples, having been on display in an exiccator in the corrosive medium of NaCl 3%.

Two groups of samples were tested for a comparative evaluation of corrosive characteristics. The first one was cleaned mechanically. The second one was processed by the hydrocleaning method with the dilatant fluid.

Results of the corrosive tests are shown in Table 2.

As it is seen from the investigation results, a weight loss value for the samples, undergone the hydrocleaning, is less than for the samples, cleaned mechanically.

This experiment proves that coating, obtained with the help of hydrocleaning with dilatant fluids, slows down the development of corrosive processes.

An important moment of our study is that not only the effectiveness of the hydrocleaning with fluids with

the effect of dilatant reinforcement, but also an inhibitive effect of a working fluid, which slows down the development of corrosive processes on the surface of processed steel works, are practically determined.

A developed methodology of a hydrodynamic cleaning has a number of undeniable advantages, such as higher economic effectiveness in comparison with dry-blasting, improved working conditions of personnel, as dust is partially washed down, and also anticorrosive protection of steel surfaces.

A proposed technology of dilatant-blasting can be widely used in many manufacturing sectors, such as: railway and motor transport; oil and gas production; refinery; community services. In other words in any production, where steel works need renovation. ♦

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«PIGMENT» DEVELOPED NEW PIGMENTS FOR PRODUCING POWDER PAINTS AND COLOURANTS

Pigment OJSC is developing new applications for its products: manufacture of thermoplastics powder paints. The Tambov-based company offers the red 5S m. B, β -modified phthalocyanine blue, and orange K. pigments. The high quality of pigments intended for such applications has been validated during laboratory tests. All these products comply with international standards and can be offered as an alternative to the best European analogues.

Pigments for colourants represent yet other addition to «Pigment» product portfolio. In particular, the company's recent designs include the phthalocyanine blue 15:3 pigment for water-based colourants. This pigment allows increased utilisation during grinding and, accordingly, energy consumption during manufacture of paints to be reduced by 15-20%. Test confirms the product's environmental safety.

It should be noted that Tambov-based Pigment OJSC is currently the sole manufacturer of organic pigments in Russia and the CIS, while the company itself has been active in the market for more than 65 years.

<http://www.krata.ru>

RUSAL DEVELOPS ITS ALUMINIUM POWDER BUSINESS

The Volgograd Aluminium Smelter has been integrated into Rusal's ambitious modernisation programme aimed at developing its aluminium powder business. The project intended to boost the aluminium products output and involving \$52m of investments will be implemented in the company's two production sites: in Volgograd and in Shelekhov, Irkutsk Area.

According to the Volgograd Area Ministry of Industry and Trade, the programme is scheduled to complete in 2022, aiming to increase the aluminium powder output from 20 thousand to 25.5 thousand tons annually, which would give the company a 76% share of the Russian and CIS markets.

Investor funds will be used to develop state-of-the-art technologies of «dry» and «wet» grinding that would allow the



company to enter a new market segment – aluminium paste. In addition, the launch of new types of foaming agents for aerocrete, as well as of high-tech pigments for paints is expected.

It should be noted that the Volgograd Aluminium Smelter's powder line is ranked among the most promising areas: in 2013 and 2014, investments in the production development at the plant already amounted to \$2.7m.

Aluminium powders are used in the manufacturing of paints, cellular concrete, refractories, plastics, solar panels, explosives. The key consumers include the metallurgical, chemical, power, construction, mining, and military space industries.

<http://www.rusal.ru>

RUSSKIYE KRASKI: THE COMPANY'S 2014 RESULTS

Total sales of paints by Russkiye Kraski in 2014 amounted to 4,902m roubles (a slight increase of 2.5% above the 2013 figures).

Total output was about the same as last year's at 30,505 tons. Losses mostly occurred in decorative and OEM coatings, while positive dynamics was observed in the manufacture of industrial, water-based and powder paints.

Sales of decorative paints were 1,203m roubles – same as in the previous year. Sales growth was restrained to a certain extent due to the product portfolio reallocation between solvent-based paints and water-based paints in favour of the latter.

Sales of car repair paints totalled 1,316m roubles – slightly higher compared to the previous year. Sales of paint mixing systems and the effect enamel group continued to grow. Good growth dynamics was observed in the primers and coatings group distributed under the Guntex brand name.

The industrial paints sector has also been developing fast with sales of 710m roubles, excluding sales of OEM materials. Most of the growth occurred in the group of anticorrosive paints sold under the Prodecor brand name. Sales of OEM materials have shown a drop due to declining production volumes in the automotive industry.

A total of 887m roubles' worth of powder paints was sold (+28% compared to 2013). Positive dynamics has been demonstrated across almost all segments of powder materials applications.

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PIGMENT OJSC OUTPUT GROWS BY ALMOST 19%

2014 was another year of success for Pigment OJSC, marked by increased production and sales volumes. In monetary terms, these figures exceeded 5.9bn roubles, which is almost 19% more than in the previous reporting period. Over the past 12 months, Pigment produced more than 117 thousand tons of various chemical products, which is 12.5 thousand tons more than in the previous year.

Compared to 2013, production volumes of optical brighteners increased last year by almost 60%, those of petrol additives – by 10%, synthetic resins – by 25%, formalin – by 23%, acrylic dispersions – by 34%, organic pigments – by 4%.

Exports increased by 26%. More than 14 thousand tons of products worth 800m roubles were shipped to the neighbouring countries and beyond.

In 2014, more than 364m roubles were invested in the company's development. Most of these funds were spent on upgrading the power system, as well as on increasing production capacity for acrylic dispersions, which had a positive effect.

Nature conservation is also an important area of activities for Pigment OJSC. In 2014, more than 30m roubles were allocated for this purpose. As part of the activities in this area, sewerage network was rebuilt, sewage ponds were upgraded, sludge reservoirs were reclaimed and other steps were taken, which allowed for the amount of industrial waste to be significantly reduced.

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