УДК 678.4.023

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PERFORMANCE OF COATINGS POLYESTER POWDER PAINT

The change of physical-mechanical properties of powder polyester paints under the influence of UV radiation was investigated. The regularity of changes in the properties of paints depends on the chemical structure of the pigment used. On the basis of results of the research powder polyester paints of different colors, highly resistant to weathering were developed.

Key words: polyester paint, UV radiation, the pigment.

Introduction. Among the most important service properties of paint coatings are physical and mechanical (impact resistance, bending resistance, adhesion, hardness, resistance to wear); decorative (preservation of initial layout, color, gloss, resistance to chalking); corrosion resistant (resistance to water and water solutions of salts, acids, alkali, salt spray); weather resistance (ability to withstand climatic factors). The results of climatic resistance trials for powder polyester paint coating of different colors were published earlier [1].

Powder paints consist of: film-forming agents (oligomers), hardeners, hardening agents, filling agents, pigments and additives. Powder paints can be either colored or colorless. Pigment is the component responsible for color and its steadiness. The better is the quality of pigment the longer the painted surface will have its initial layout. Colorless powder paints are called lacquers.

Composition and technology for the production of the developed polyester powder paint were considered in paper [2].

During the tests of powder polyester paint coating operational properties paints with different pigments were used.

When selecting pigments the following concepts were taken into account. Phthalocyanine pigments are universal and fit for painting any polymer materials. Exclusive resistance and relatively low price guarantee their wide use and tendency to displacement of other blue and green pigments. Blue and green phthalocyanine pigments have excellent pigment properties. Blue pigment has coverage of 4–5 g/m², its coloring power exceeds iron blue by 2-3 times, heat resistance to 200°C, light resistant, resistant to acids, alkali, all kinds of filmforming agents, pH = 6-9 (aqueous extract), density 1.62 g/cm³. Green phthalocyanine pigment in contrast to a blue one contains 14-15 atoms of chlorine in a molecule that displaced hydrogen atoms on the exposed faces of crystals. B-form of pigment is of bright green color. It has extremely high resistance to any exposure but it has reduced coloring power in comparison to a blue one, pH = = 6-9 (aqueous extract), density 2.14 g/cm³.

White pigment is titanium dioxide of rutile crystalline form that is more weather resistant in comparison to anatase form. Rutile TiO₂ is 30% more covering than the anatase one.

Titanium dioxide is chemically inert: insoluble in weak acids and alkali, insoluble in organic solvents.

Black pigment is carbon black (soot), density $2.0-2.2 \text{ g/cm}^3$, bulk density $80-150 \text{ kg/m}^3$, coverage $3-6 \text{ g/m}^2$, pH = 2-6 (aqueous extract).

Carbon black is heat resistant, resistant to acids and alkali. To prevent dusting and increase in bulk density carbon black is granulated.

Red pigment diketopyrrol-pyrrol refers to the class of polycyclic pigments. It is resistant to high and low temperature; it has good chemical, light and weather resistance.

Paint manufactured based on organic pigments has low coverage, that's why during filling these pigments shall be used in combination with inorganic pigments or fillers, most often titanium dioxide or barite.

Optimal content of colored (organic or inorganic) pigments in compositions varies (depending on intensity and required coating color) from values less than percent to some percents.

Main part. Preparation of base for painting and preparation of protection coatings were carried out in compliance with GOST 8832–76.

Steel plates were cleaned and degreased by acetone (xylol) and soft cloth, processed by sandpaper with grain size 5 or 4 and again cleaned by organic solvent, if necessary, dried in the heat chamber.

Glass plates were cleaned by organic solvent and cloth and baked in the heat chamber at 120°C.

Hardness and gloss of the coating were determined using special glass plates with dimensions of 90×120 mm and thickness of 1.2-2.0 mm. Coating flexural resilience was determined using black tin plates with dimensions of 20×150 mm and thickness of 0.8-1.0 mm.

As a base the samples of asbestos slate with dimensions of 200×150 mm manufactured by Production Republican Unitary Enterprise "Krichevcementnoshifer".

The coating of asbestos slate was cleaned mechanically to remove dust and foreign particles.

The samples of asbestos slate previously to painting with powder paint were heated in the chamber for 30 min at 180°C, then cooled to 50°C. Preheating is required to reduce the air content in pores better and provide the better adhesion of powder paint on the surface. The paint was applied on the front surface in two layers by Start-50 spray gun using electrostatic spraying method. Metal samples were painted by powder paint in one layer without preheating.

For coating formation ShS-80 cabinet dryer was used.

The hardening of powder paint was carried out at the temperature of substrate of 180°C and time in kiln of 20 min.

Coating thickness after hardening was $60–80~\mu m$ for metal.

Coating thickness on steel and tin plates was measured using Konstanta-K5 portable digital electromagnetic thickness tool (JSC "Konstanta", the Russian Federation).

On glass plates the thickness of coating was determined by measuring thickness using MR-25 micrometer according to GOST 4381-87 with error of ± 3 µm, removal of a part of coating and measurement of the plate thickness in this area without coating. The result of measurement was considered to be the arithmetic mean of 5–6 determinations. The operational properties of coatings were determined using the following methods: adhesion according to GOST 15140-784 (ISO 2409); abrasive wear resistance according to GOST 8747– 88; impact resistance according to GOST 4765-73 (ISO 6272); bending resistance according to GOST 6806-73 (ISO 1519); Buchholz hardness according to DIN 53153, ISO 2815; gloss according to GOST 896-69 (ISO 2813); color fastness according to GOST 11583-74, STB 1118-98 (measurement No. 1); salt spray resistance according to GOST 9.308-85 (ISO 9227); water resistance according to GOST 9.401-91 (ISO 6270); cupping test according to ISO 1520, DIN 53153.

As one of the main factors destroying the protective coatings operated in atmospheric conditions is the effect of ultraviolet sun radiation, its effect on the change of the properties of powder paint coating with different pigments was estimated.

In this paper the effect of UV radiation on five coating compositions of polyester powder paints with different pigments applied on metal base and three coating compositions of polyester powder paints with different pigments applied on asbestos slate base were investigated.

With this purpose the samples with polymer coating were exposed to S 1200 decoy emitter (Germany) for 1,200 and 2,400 h. Irradiation energy was correspondingly 4,786 and 9,572 MJ/m² at cumulative integral flux of 1,107.7 W/m².

The initial gloss of polymer coatings of different colors is indicated by the following values, %: red – 80.1; green – 85.6; blue – 82.7; white – 94; black – 89.6. The change of the gloss of coatings of different colors after UV exposure for 1,200 and 2400 h were detected, the results are provided on Fig. 1.

According to the data of the study the change of the gloss of coatings took place in the following way.

After 1,200 h of irradiation the gloss of coatings reduced insignificantly in the films of white and blue color for 1.2 and 2.5%, respectively. 4.2% for the coating of red color. 6.1% for the coatings of green and black color.

After 2,400 h of UV exposure the change of the gloss of coatings took place in the following way. The biggest reduction of gloss was observed in the coating of black color -9.4%, equal in white and green -8.2%, red -7.9% and blue -6.3%.

On average the loss of gloss for all samples in comparison to those not subjected to UV exposure was 10%, thus corresponding to the requirements for powder paints.

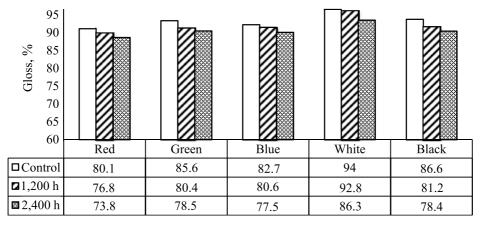


Fig. 1. Changes in the gloss of polymer coating after UV exposure at an angle of 60°

Analysis of the obtained results is confirmed by the data [3]. In the process of prolonged operation in atmospheric conditions and subjected to light exposure due to the photochemical activity of pigments the formation of the layer of the destructured film forming agent takes place, thus causing the erosion of coating, i.e. chalking. This macroprocess is controlled through the change of the gloss of coatings in the process of ageing.

Color fastness is an important parameter for paints if to speak about the stability of the white and colored pigments. The method is based on the determination of color coordinates for the studied samples using color comparator and calculation of color differences between the initial sample and the sample subjected to light illu-mination.

The values of color (colorimetric) specifications ΔE (ΔL , Δa , Δb) provided in Fig. 2, speak of high color fastness of all pigments.

Values ΔE after 1,200 h of UV exposure for red, green, blue, white and black colors are: 3.91; 1.18; 0.38; 0.36; 0.58 conv. u., respectively, and after 2,400 h of UV exposure - 4.21; 1.62; 1.04; 0.58; 0.59 conv. u., respectively. ΔE does not exceed four thresholds of color sensitivity, with the exception of the red color after 2400 h of exposure.

So the pigments with decorative functions in coatings used by us have the required fastness (ability to preserve color stability, gloss and brightness under light illumination [3]). The resistance of pigments to photochemical degradation depends both on their molecular structure and on chemical properties of film forming agent where they are distributed. In our case where the same film forming agent is used the light resistance of pigments is to a great degree related to their reflecting power, mainly in the short wave part of the visible spectrum and in the UV spectrum. Soot intensively absorbs in the visible spectrum, however it reflects well in the UV spectrum, thus it is one of the most light-resistant pigments. Titanium dioxide intensively absorbs in the UV spectrum, thus its light resistance decreases during prolonged exposure.

Light resistance of pigments is also affected by their crystalline structure and dispersion ability.

Coarse crystalline structure of pigments is more light resistant as corners and edges of small crystals form great numbers of initial centers of photodegradation reaction [4].

The reason for high light resistance of phthalocyanine pigments lies in the symmetric structure of their molecules that are composed of four remainders of isoindole forming the closed 16-member ring. Atom of copper located in the center of the molecule and bound by covalent and coordinate bonds with atoms of nitrogen imposes a stabilizing effect on the whole molecule [5]. The central atom of copper in β -form crystals of blue pigment has an octahedral site in relation to subjacent and superjacent aromatic and cyclic fragments of the molecule that's why intramolecular influence is stronger and light resistance is higher in contrast to the α -form.

Green phthalocyanine pigment in contrast to the blue one contains 14–15 atoms of chlorine substituting hydrogen atoms on exterior edges of crystals thus providing some hydrophilic properties for the surface upon preservation of high light resistance [5].

It is known [4, 5] that introduction of pigments increases the light resistance of paint coatings at the cost of blocking some light beams through their reflection, absorption or dissipation. As a result the film-forming agent under the layer of pigment particles is not subject to the effect of light and ageing. Of special efficiency in this relation are sheeting pigments with scale-like particles (aluminum powder, mica).

On the other hand many pigments have photochemical activity in relation to film-forming agents. It leads to the increased ageing of coatings based on the following two mechanisms.

Photo mechanism. Resistance of non-pigmented polymer coatings to light ageing is relatively high. As usual solar radiation (visible spectrum, $\lambda = 370-720$ nm) has no energy to disrupt chemical bonds in a film-forming agent in a fast way.

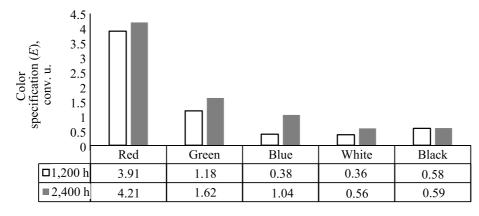


Fig. 2. Color fastness of polymer coatings after UV exposure

The other situation is in the case of pigmented coatings. In photochemically active pigments under the effect of emission of $\lambda = 370-720$ nm (daylight) the mass transition of electrons to a higher energetic level takes place. At the reverse transition of electrons the electromagnetic oscillations of $\lambda < 370$ nm are generated that destroy the film forming agent in close vicinity to the pigment surface.

Photochemical mechanism. Under the effect of light some pigments has the ability to recover with the emission of oxidizer that causes the oxidative decomposition of the film-forming agent:

$$2\text{TiO}_2 \stackrel{h\nu}{\longleftrightarrow} \text{Ti}_2\text{O}_2 + \text{O}.$$

As a result of the decomposition of film-forming agent around pigment particles the area of the decomposed film-forming agent is created and the chipping of pigment particles off the coating at insignificant abrasive effect is observed, i.e. chalking, thus leading to significant reduction of protective and decorative ad mechanical properties of the paint coating.

The photochemical activity of pigments depends on their chemical nature, size and shape of particles, parameters of crystalline structure and its imperfection. The effect of dispersion ability is grounded by the alteration of the surface area where photochemical reactions in the pigmented coatings take place.

For example, the optimal form for zinc oxide particles is the acicular shape.

The effect of crystalline structure parameters, impurities, defects is determined by the change of the energy of electron transitions. Those pigments with dense crystalline lattice, minimal defects and

impurities have minimal photochemical activity. In order to reduce photochemical activity the surface of pigments is treated by salts ad oxides of heavy metals (Zn, Ca, Al, Cu, etc.). The pigments with increased photochemical activity (anatase form of titanium oxide) increase the decomposition of coatings. In contrast to that the pigments shielding the irradiation (carbon black) slow down ageing [4–6]. The decomposition of coatings under the effect of sun light starts with the surface layer. After the determination of the spectral distribution of the energy of irradiation absorbed by the coating under the effect of sun light it was discovered that approximately 90% of the energy of ultraviolet irradiation is absorbed by the surface layer with the thickness of 5–10 µm [7].

During ageing of the pigmented coatings the structure-forming processes lead to the aggregation of pigment particles and appearance of significant tension around large component aggregates.

Photooxidation processes are more likely on the borders of structural formations. In this relation the increase of internal tension leads to the increase in the bond-breaking in macromolecules, increase in the reaction of radical decomposition thus stimulating the decomposition of coatings [7] and reduction of their physical and mechanical properties.

The tests of the alteration of polymer coating properties after light ageing were conducted. Physical and mechanical properties of polymer coating on metal plates were assessed by the following parameters: Buchholz hardness; adhesion; impact strength; cupping test. The obtained results are provided in Table 1. The analysis of the data of Table 1 demonstrates the following.

Table 1 Alteration of technical and mechanical properties of coatings of different colors exposed to UV irradiation

Parameter		Coating color				
	red	green	blue	white	black	
Impact strength, cm:						
control sample	100	70	75	60	65	
– after 1,200 h of UV irradiation	100	60	70	40	50	
– after 2,400 h of UV irradiation	100	50	50	40	45	
Cupping test, mm:						
control sample	10.9	10.0	8.9	9.8	8.2	
– after 1,200 h of UV irradiation	10.2	9.0	8.1	9.4	7.6	
– after 2,400 h of UV irradiation	9.4	7.5	7.2	8.9	6.9	
Buchholz indentation (hardness), conv. u.:						
– control sample	90.9	90.5	90.9	76.9	83.3	
– after 1,200 h of UV irradiation	84.2	73.4	89.3	70.8	70.5	
– after 2,400 h of UV irradiation	76.9	71.4	88.9	66.7	62.5	
Adhesion, points:						
– control sample	1	1	1	1	1	
– after 1,200 h of UV irradiation	1	1	1	1	1	
– after 2,400 h of UV irradiation	1	1	1	1	1	

According to the data of the tests after 1,200 h of irradiation the impact strength reduced in al coatings. For the coating of red, green and blue color this parameter reduced for 12.2; 14.3; 13.3% respectively, for white and black color – for 33 and 23%.

Upon the twofold increase of irradiation time to 2,400 h the impact strength of the coatings of red, green and blue color reduced twofold and for the coatings of white and black color this parameter reduced by a factor of 1.5.

It shall be noted that polymer coatings are resistant to the impact from the height of 60–100 cm and that exceeds the value indicated in the technical specifications (not less than 50 cm).

Let's point out that film's impact strength is a standardized parameter. This parameter is included to almost all technical specifications for almost all paint materials.

The impact strength of coatings is dynamic hardness of coating and the tensile strength of coating is static strength of coating.

One of the main characteristics determining the service life and corrosion protection of any coating is coating's deformation strength.

Cupping test is one of the most important in testing set. In the process of squeezing the static loads affecting the coating in the process of its operation are simulated.

The results of cupping test for coatings after 1,200 h of irradiation are the following. The coatings of red, green, blue, white and black colors this parameter reduced correspondingly for 6.4; 10.0; 8.9; 4.1; 7.3%. After the increase of irradiation time to 2400 h the reduction of hardness at cupping test for all samples is the following: red, green, blue, black colors are characterized by reduction for 13.8; 25.0; 19.1; 9.2; 15.8% in comparison to control samples.

According to Buchholz hardness test the coating of all colors are also characterized by the reduction of this parameter after irradiation (Table 1).

The analysis of the obtained results (Table 1) demonstrates that the alteration of hardness parameters of coating is related to the start of the degradation of coatings. As a result of light ageing of coatings the processes of photooxidation on the borders of structural formations are highly probable. I this relation the increase of internal tensions leads to the increase in the bond-breaking in macromolecules, increase of radical decomposition reaction, thus leading to decomposition of coatings [7] and reduction of their physical and mechanical properties.

Adhesion is considered to be the result of the formation on the base surface of the oriented layer of molecules of film-forming substances. The formation of the oriented layer is the result of the sur-

face absorption of the ends of molecules of filmforming substances and adhesion in this case is increased at the increase of the polarity degree of the molecules of film-forming substances.

The adhesion strength of paint materials is affected by internal tensions: the higher the tensions the lower the adhesion.

The results of the tests for adhesion strength determination of control coatings and coatings after UV irradiation did not demonstrated the reduction of the aforementioned parameter.

All control tested samples have adhesion equal to zero (ISO 2409).

From the data of corrosion resistance of the coatings of domestically produced powder polyester paint (Table 2) it can be seen that the coating has high water resistance: it has no visual changes after exposure for 1,000 h in the climatic test chamber at 40°C and maintenance of air humidity condensation on it.

After tests in aggressive liquid media (water, 5% solution of NaCl, 3% solution of Na₂CO₃) the plates protected by the coating from both sides and ends were submerged in the vessels with fluids than the vessels were sealed. The samples were incubated at 20° C for 500 h.

Table 2
Corrosion resistance of metal coating represented
by powder polyester paint PPK-01 RAL9005
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Parameter	Value	Test methods
Water resistance at (40 ± 2) °C, for 1,000 h,	No alterations	GOST 9.401–91
Resistance to exposure to liquids at $(20 \pm 2)^{\circ}$ C, for 500 h:		
– water	No alterations	GOST 9.403–80
- 5% solution of NaCl	No alterations	GOST 9.403-80
- 3% solution of Na ₂ CO ₃	No alterations	GOST 9.403-80
Salt spray test, for 1,000 h	No alterations	GOST 9.308–85

At the assessment of the coating condition the following possible types of its decomposition were recorded: blubs, film exfoliation, film shrinkage, corrosion destruction of metal, film dissolving. After 500 h of exposure none type of decomposition was detected thus corresponding to the requirements of GOST 9.401–91.

Salt spray test is a widely accepted corrosion test. The test was conducted in accordance with GOST 9.308–85 (ISO 9227).

As according to ISO 9227 corrosion shall not be visible for 500 h the powder polyester paint developed by us provides increased corrosion resistance for protective coatings.

Test results of the corrugated asbestos-cement sheets with polymer coating

Parameter name, technical requirements, specifications	Values	
Outward appearance (color coordinates and uniformity of color)		
Blue color: uniformity of color ΔE (Δa , Δe , ΔL)	1.6114; 1.5618; 1.7986; 1.5680	
Green color: uniformity of color ΔE (Δa , Δe , ΔL)	0.7167; 0.8312; 0.9014; 1.0094	
Burgundy color: uniformity of color ΔE (Δa , Δe , ΔL)	0.8994; 1.0054; 0.9654; 0.2955	
Adhesion of polymer coating to asbestos-cement sheet, MPa	3.2	
	(cohesive nature of fracture)	
Abrasive wear resistance	No integrity damage	
	for polymer coating	
Color fastness of polymer coating after accelerated climatic ageing for 168 h:		
– blue color	$\Delta E (\Delta a, \Delta e, \Delta L) = 1.47$	
– green color	$\Delta E (\Delta a, \Delta e, \Delta L) = 1.67$	
– burgundy color	$\Delta E (\Delta a, \Delta e, \Delta L) = 1.64$	
Resistance to statistic water exposure for 24 h, alteration of outward appearance:		
– blue color	$\Delta E (\Delta a, \Delta e, \Delta L) = 0.02$	
– green color	$\Delta E (\Delta a, \Delta e, \Delta L) = 0.01$	
- burgundy color	$\Delta E (\Delta a, \Delta e, \Delta L) = 0.02$	

Physical and mechanical and operational properties for polymer coating on asbestos slate were assessed by the following parameters:

- adhesion bond strength;
- abrasive wear resistance;
- color fastness;
- resistance to water static exposure.

At the selection of color palette the most popular colors of roof coatings were taken into account (blue, green, burgundy) used in construction.

In order to assess the color fastness of the colored polymer coating on asbestos slate after the exposure of light irradiation (artificial ageing) the following parameters were monitored: color differences ΔE between the baseline and exposed samples; alteration of adhesion strength (adhesion); abrasive wear resistance (Table 3).

The cumulative integral flux of optical emission from decoy emitter S 1200 at the distance of 60 cm from the emission source was 1,107.7 W/m².

The value of irradiation energy for the samples from the decoy emitter for 168 h was 670 MJ/m².

The polymer coatings of asbestos-cement sheets after the accelerated climatic ageing for 168 h remain color fast. Maximum color difference ΔE for colored polymer coating is 1.47 to 1.67 and according to STB 1,118 the value of ΔE shall not exceed 3.0.

Table 3 contains the results of the tests of asbestos-cement sheets with polymer coating. The tests for abrasive wear resistance of the polymer coating of asbestos slate with polymer coating demonstrated that the control samples and samples subjected to tests have no alterations of the outward appearance of polymer coating.

During the test for resistance to static water exposure almost no alteration of the color of polymer coating is observed, color difference ΔE equals 0.01–0.02.

As a result of tests it was established that adhesion of polymer coating to asbestos-cement sheet is 3.2 MPa on average and the type of fracture on sample is cohesive fracture.

The results of the conducted tests demonstrated that polymer coating on asbestos slate corresponds to the requirements set for physical and mechanical and operational parameters in the normative and technical documentation of STB 1118-2008 "Corrugated asbestos-cement sheets and their parts. Alteration No. 1" and can be used for the finishing of asbestos slate.

Conclusions. Powder polyester paints of different colors were developed (red, green, blue, white and black) in order to create protective decorative coatings on asbestos slate and metal. These coatings have a set of wonderful properties: glow, color fastness, light resistance, adhesion, impact strength and tensile strength, hardness, water resistance, resistance to aggressive liquids and salt spray. The developed polyester powder paints correspond to all the requirements set for paint materials of this class. The effect of the chemical structure of pigments, shape and size of their particles not only on decorative properties of coatings but on the process of their light ageing was demonstrated.

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Received 24.02.2015