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FORMATION OF POWDER COATING PROPERTIES IN THE SYSTEM "FILM-FORMING – CROSS-LINKING AGENT"

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Abstract. The results of the influence of film formers of different types on the formation of the properties of powder paints and coatings based on them was showed. Powder coating are one of the most promising types of paints and varnishes for industrial use. Their main advantages are the absence of solvents, virtually waste-free coating technology (the degree of utilization of the powder in the application is close to 100 %), relative simplicity and efficiency in the production process of the coating. As a result of study it has been revealed that the use of powder coating systems of different chemical nature provides higher physical and mechanical characteristics of coatings in comparison with traditional systems based on liquid acrylic resin, which in its turn allows to consider such systems as an alternative for protection of construction metal products and structures against the mechanical influences. At the same time, it has been shown that a change in the film former and crosslinking agent in the composition of powder systems differently influences the formation of powder coating properties depending on the type of the film former and its characteristics (viscosity, glass transition temperature) as well as the type of the crosslinking agent. The use of systems "polyester film forming – TGIC", "polyester film forming – HAA" provide high physical and mechanical properties of coatings without deterioration of technological properties of systems, when using film forming with dynamic Brookfield viscosity values within 30^{o}C). In turn, the decrease of the glass transition temperature index and the increase of the resin viscosity index negatively affect the formation of the technological properties of the powder systems and, accordingly, the physical and mechanical characteristics of the coating.

Keywords: powder coating, film forming, crosslinking agent, coating, adhesion, bending strength, impact strength, pulling strength.

Introduction. The formation of quality coating coatings with a long service life without environmental degradation during their application is largely determined by the composition and physical and mechanical properties of coating materials [1].

Paint-and-varnishes materials differ fundamentally from typical products on the Ukrainian market by the content of solvents up to 40 %, which inevitably leads to their emission during the production and application of coating as well as to the environmental pollution [2]. In this case, the reasonability of reduction in using paint-and-varnishes materials based on solvents in Europe was caused by the Directive 1999/13/EC that does not allow producing materials with emissions of organic solvents exceeding set limits and Directive 2004/42/EC concerning paint-and-varnishes products that imposes new restrictions on the content of volatile organic substances in certain products and materials such as paint-and-varnishes coatings.

The actual direction from the practical and scientific point of view is the increase in the use of coating compositions that do not contain any organic solvents, heavy metals and other harmful substances. The most promising coating material for the protection of metal building products and structures is the use of powder paints [2]. High prospects for the use of powder coating materials are explained by their ecological completeness and attractiveness in terms of the legislative strictness of environmental protection to reduce emissions of volatile organic compounds (VOC), as well as their high efficiency associated with the possibility of obtaining high quality decorative and protective coatings with high weathering and chemical resistance when applied in a single layer [3, 4].

The introduction of powder coating materials for the protection of building metal products and structures with a long service life requires the study of the features of the formation of powder coating properties, taking into account the influence of film-forming components and cross-linking agents.

Analysis of recent research and publications. Chemically there are two groups of raw materials for the production of powder coatings: thermoplastic-based and thermosetting film-forming [5]. Thermoplastic film-forming form coatings without chemical transformations, mainly due to melting of powder particles and cooling of melts – thermoplastic. During curing of powder coatings based on thermosetting film-forming a cross-linking reaction of the coating system occurs in the presence of catalysts, which leads to the use of polymers with significantly lower molecular weight and accordingly lower melt viscosity. As a result, the high content of pigments and fillers can be successfully dispersed and included in the system of thermosetting coating material, contributing to the high quality of the product at its low cost [6, 7].

At the current stage of development, the volume of world production of thermosetting powder coatings is about 80% of the total output of powder coating materials, which proves their efficiency [8]. Materials of this group are made on the basis of film-forming oligomers promoting the obtaining of high-quality coatings with thickness of 30...80 microns which has determined their high competitiveness in comparison with coatings on the basis of liquid paints [9].

The formulation of a thermosetting powder coating consists of five basic components: thermosetting oligomer (film-forming agent), crosslinking agent, pigments, fillers and functional additives [10, 11]. In general, the film-forming agent and the crosslinking agent play the main role in providing the necessary mechanical characteristics and durability of the powder coating. At the same time the question of the influence of film-forming on the formation of physical-mechanical and operational properties of the powder coating depending on the type, chemical structure and main characteristics (viscosity, glass transition temperature) remains open.

Taking into account the large volume of thermosetting powder coatings production in the world it is reasonable to study the influence of film-forming of different types on the formation of properties of powder coatings and coatings based on them.

The purpose of this paper is to investigate the influence of film-forming on the formation of powder coating properties.

Research materials and methods. Rationale for selection of raw materials for obtaining powder coatings based on them.

When carrying out the research, the heat-curing oligomers of various types, chemical structures and basic characteristics (Table 1) in the form of epoxy, saturated carboxylic polyester and hybrid resins, which are the most common representatives of binders for the possibility of obtaining powder coating systems, were used as film-forming substances, namely:

– carboxylic term polyester resins Crylcoat 2441-3, Crylcoat E04484 by Allnex, EP-2105 by KHUA, to produce polyester systems using the TGIC crosslinking agent;

– carboxylic polyester resins Crylcoat 2618-3T by Allnex, GP 95518/T by Ciech, EP-3126T by KHUA, Alymers PC2812T by Inopol to obtain polyester systems using the HAA crosslinking agent;

– carboxylic functional polyester resins Crylcoat 1771-3T by Allnex, GS 7371/T by Ciech to obtain hybrid systems;

– epoxy resins Epidian 033A from Ciech; D.E.R. 663 EU by Dow, CHS 130 by Spolchemie to obtain epoxy and hybrid systems.

The following substances were selected as crosslinking agents depending on the type of film former: for carboxyl-containing polyester resins forming the polymer matrix by step polymerization, crosslinking agents in the form of Triglycidyl isocyanurate (TGIC) and Hydroxyalkyl Amide were used; for epoxy resins, a typical representative crosslinking agent among aliphatic solid amines in the form of Dicyandiamide (DICY) was used; for carboxylic polyester resins, Bisphenol A epoxy resin was used.

Table 1 – Properties of the film-forming component

Type of the resin	Indicators				
	Glass transition temperature, ºC	Brookfield viscosity 200ºC, mPa.s	β value	Acid value (mg KOH/g)	Curing schedule
Polyester film-forming with TGIC					
Crylcoat 2441-3T	67	4200	15	34	200C 10хв
Crylcoat E04484	65	5500	10	37	200C 10хв
EP-2105	68	4500	12	30	200C 10хв
Polyester film-forming with HAA					
GP 9518/T	61	3200	13	35	180C 10хв
Crylcoat 2618-3	61	3400	10	35	180C 10хв
EP-3126	61	3000	12	28	180C 10хв
PC2812T	58	3100	11	31	180C 10хв
Polyester film-forming for hybrid systems 70/30					
Crylcoat 1771-3	56	4500	15	35	180C 10хв
GS 7371/T	57	5500	16	32	180C 10хв
Epoxy film-forming					
CHS 130	–	800	32	10	200C 10хв
Epidian-033A	–	1200	31	13	180C 10хв
D.E.R. 663UE	–	900	30	11	180C 10хв

The compositions of the studied systems using the selected film-forming substances and crosslinking agents are given in Table 2. A liquid paint system based on alkyd resin (Urakyd) was used as a control composition.

In general, the following systems were used:

– "Polyester film former – Triglycidyl isocyanurate";

– "Polyester film former – Hydroxyalkyl Amide";

– "Polyester-epoxy film former";

– "Epoxy film former – Dicyandiamide" (control);

– "Alkyd film former" (control).

The study of the properties of decorative and protective powder coatings using different groups of modifying additives was carried out in the following sequence:

1. Powder coating systems were applied to plates (size 150 × 60 mm) made of St3 steel. The systems were applied electrostatically according to ISO 1514:2016 using a Start 50 spray gun.

2. Curing of powder coating on samples-plates based on the known data regarding polymerization modes [12] was carried out in a curing chamber at 180ºC, 10 min for the systems: "Polyester film former – Hydroxyalkyl Amide", "Polyester-epoxy film former"; 200ºC, 10 min for the systems: "Polyester film former– Triglycidyl isocyanurate"; "Epoxy film former – Dicyandiamide" systems.

3. Determination of the resistance of coatings to return impact is performed according to DSTU ISO 6272-2:2015 [13]. The purpose of this test is to test the rapid deformation of powder coatings and evaluate their resistance to cracking and/or peeling from the painted surface when they are subjected to deformation under the influence of falling load of a given weight with a spherical striking edge.

4. Determination of bending strength of coatings was performed according to DSTU ISO 1519:2015 [14]. The purpose of this test is to evaluate the resistance of powder coatings to cracking and (or) peeling from the substrate to bending, by bending the tested coating plates around a cylindrical rod using a test instrument equipped with a set of hinges, each of which is connected to a cylindrical rod of appropriate diameter.

5. Determination of coating drawing strength was determined according to DSTU ISO 1520:2015 [15], according to which the resistance of powder coating to cracking and/or peeling from the metal surface at a constant punch indentation under standard conditions was evaluated.

6. Adhesion of the coating by pull-off test is defined according to DSTU ISO 4624:2019 "Paints and varnishes. Determination of adhesion by pull-off test" [16].

Table 2 – Composition of powder coating system

Compo Sition №	Name	Content of raw materials,%	
		Film-forming	Crosslinking agents
Polyester film-forming with TGIC			
1	Crylcoat 2441-3T	93	7
2	Crylcoat E04484	93	7
3	EP-2105	93	7
Polyester film-forming with HAA			
4	Crylcoat 2618-3	94	6
5	GP 95518/T	94	6
6	EP-3126	94	6
7	PC2812T	94	6
Polyester film-forming for hybrid systems 70/30			
8	Crylcoat 1771-3 – Epidian 033A	70	30
9	GS 7371/T – Epidian 033A	70	30
10	GS 7371/T – D.E.R. 663EU	70	30
11	Crylcoat 1771-3 – D.E.R. 663EU	70	30
Epoxy film-forming			
12	CHS 130 – DICY	94	6
Liquid alkyd system (control composition)			
13	Urakyd		

Note: The additive of rheological action in the form of filling agent Resiflow PV88 by Estron chemical in the amount of 1% and a degasser in the form of benzoin by Estron chemical in the amount of 0.6% were introduced into the systems (over 100% by weight of components).

Research results. According to the results of the study, it was found that the physical-mechanical and decorative characteristics of the coating systems under study change significantly depending on the type of film formulation and its main characteristics, as well as on the crosslinking agent. Thus, the coating based on the liquid alkyd system (control composition) is characterized by the following properties: back-impact strength is 20 cm/kg (Fig. 1), bending strength around a cylindrical rod is 12 mm (Fig. 2), drawing strength is 4.6 mm (Fig. 3), adhesion by the lattice notch method is class 0, adhesion by the tear-off method is 9 MPa (Fig. 4). At the same time, the coating based on powder epoxy system (CHS 130 + DYCY) is characterized by a reverse impact strength of 60 cm/kg, which is 200% higher compared to the alkyd system, while there is a 33% increase in the bending strength around the cylindrical rod, and a 13% increase in the drawing strength. The tear-off adhesion of epoxy systems is 15 MPa, which is also 65% higher. This may be due to the fact that in the process of film formation of epoxy systems under the influence of high temperatures, from the melt as a result of physical sorption and chemisorption of macromolecules on the active centers of the substrate surface are formed strong interphase connections on the border of the film – metal turn contributes to obtain high physical and mechanical coating properties [5].

In general, the physical and mechanical characteristics of coatings on polyester film-forming are higher compared to the traditional liquid system. However, compared to the epoxy system, the feasibility of their use varies depending on the basic characteristics of the film former and the type of crosslinking agent. Therefore, application of the system based on KHUA EP-2105 and TGIC helps to get strength to the return stroke (60 cm/kg) and bending strength (8 mm) at the level of powder epoxy system. At the same time, the drawing strength of the coating increases by 20%. In its turn the use of Crylcoat E04484 leads to a significant decrease of physical and mechanical properties of the coating, according to the following indexes: strength to the return stroke (40 cm/kg), bending strength (10 mm) and drawing strength (5.6 mm) in comparison with the abovementioned system on the base of KHUA EP-2105 polyester resin. This effect may be explained by the fact that Crylcoat E04484 polyester resin is characterized by higher viscosity indexes in comparison with KHUA EP-2105 (Table 1), which in its turn leads to the decrease of efficiency of model system film spreading over the substrate surface during coating curing process. In this case, the interaction of functional groups of polymer with active centers of the substrate deteriorated and, correspondingly, the physical and mechanical properties of the material decreased.

The use of Crylcoat 2441-3T polyester resin with reduced viscosity (Table 1) contributes to an increase in the coating's return impact strength to 80 cm/kg (Fig. 1.) compared to the control composition (20 cm/kg), and also provides high bending strength (8 mm) and recovery strength (7.4 mm). At the same time, the adhesion of the coating by the tear-off method is 15 MPa (Fig. 4), which is 71% compared to the control system based on the traditional liquid coating.

A similar tendency persists when using the system "polyester film-forming – HAA". Thus, the use of Crylcoat 2618-3 T polyester resin (viscosity – 3600 mPa-s) and HAA contributes to an increase in the return strength (80 cm/kg) and bending strength (6 mm), which is 33 % and 30 %, respectively, more compared to the epoxy powder system. At the same time, the coating adhesion (15 MPa) by the tear-off method remains at the level of the control composition (CHS 130 – DICY) and is significantly higher compared to the traditional liquid system (9 MPa).

A decrease in the viscosity index of polyester film-forming (according to Table 1) contributes to an increase in the physical and mechanical properties of the coating (Fig. 1...Fig. 4). Thus, the system based on Alymers PC2812T resin (viscosity – 3100 mPa-s) is characterized by higher indices of impact strength – 95 cm/kg and adhesion of 18 MPa, which is 15 % and 16 % higher, respectively, compared to Crylcoat 2618-3 analogue. At the same time, there is an increase in the extraction strength of the system (by 5.7%) and bending strength (by 25%). A similar pattern is observed when using the KHUA EP-3126 polyester resin with reduced viscosity (3000 mPa-s). The coating's return-impact strength is the highest of the systems examined, being >100 cm/kg, adhesion is 19 MPa, gloss is 86^{o}, and bending strength is 8 mm. The drawing strength of 7.1 mm also increases.

The main disadvantage of application of polyester resins (Alymers PC2812T and KHUA EP-3126) which are characterized by the lowest viscosity index (3000...3100 mPa-s) of the studied film-forming is deterioration of technological properties of the obtained powder. This is related to the fact that the glass transition temperature (Tg) of the powder system decreases with a significant decrease in the viscosity index of the polyester resin, which in turn leads to increased sensitivity of the system to changes in the ambient temperature during application and storage of the finished product.

Therefore, in order to ensure high physical and mechanical characteristics of polyester powder coating without deterioration of the technological properties of the system it is advisable to use the film-forming with dynamic Brookfield viscosity values in the range of 3600...4200 mPa-s (at $t=200^{o}C$).

According to the results of study of the "polyester-epoxy film former (70/30)" system it was revealed that the effect of the complex of resins polyester-epoxy on the formation of coating properties is less effective compared to the polyester ones. Thus, the use of the system based on Crylcoat 1771-3 polyester resin and Epidian 033A epoxy polyester-epoxy provides coating resistance to the return stroke at the level of 60 cm/kg, which is 25% lower in comparison with the abovementioned polyester systems. At the same time, the coating's drawing strength of 5.1 mm and bending strength of 10 mm are reduced. It should be noted that the obtained physical and mechanical characteristics of the "polyester-epoxy film former" system are higher compared to the control composition based on alkyd resin (Fig.1...Fig.4), but lower compared to the epoxy system. The use of a combination of GS 7371/T and Epidian 033A resins shows a 50 percent reduction in strength to backfill compared to Crylcoat 1771-3 and Epidian 033A and is 30 cm/kg, a drawing strength of 4.8 cm – 12 mm, adhesion of 12 MPa, which are the lowest physical and mechanical characteristics among all the systems studied. It is due to the fact that the GS 7371/T and Epidian 033A resins are characterized by high viscosity values (Table 1), which in turn leads to a deterioration in the mechanical properties of the coating.

In turn, the combination of the Crylcoat 1771-3 and D.E.R. 663 EU (with low viscosity values) resins show the highest physical and mechanical characteristics among the "polyester-epoxy film former" coating systems, which confirms the influence of the viscosity values of the resins on the properties of coatings. Thus, the coating's strength to the action of the reverse impact is 70 cm/kg, gloss of 90º, drawing (pull-off) strength of 5.9 mm, with these indicators being higher in comparison with the control composition based on the epoxy resin (Fig.1...Fig.4).

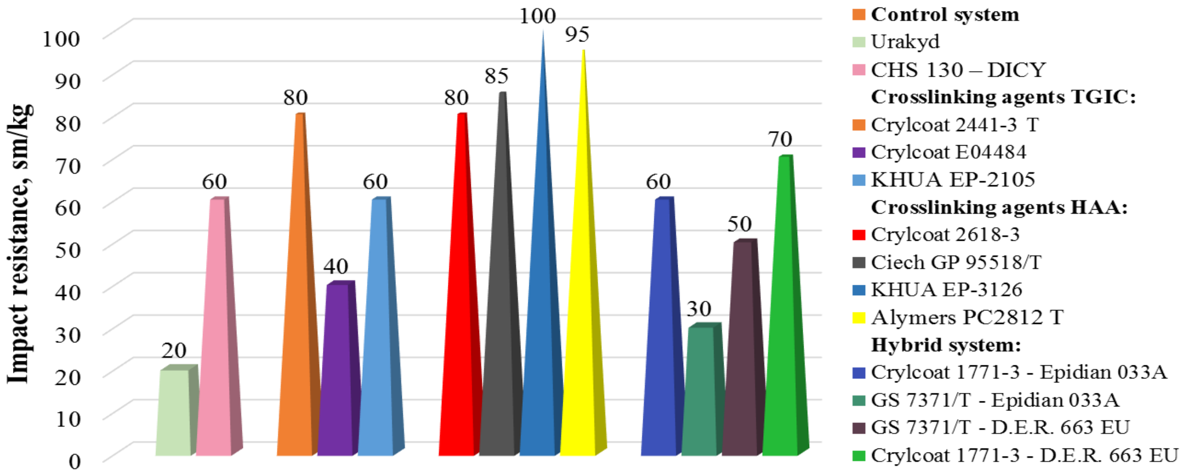

Fig. 1. Impact resistance of the powder coating

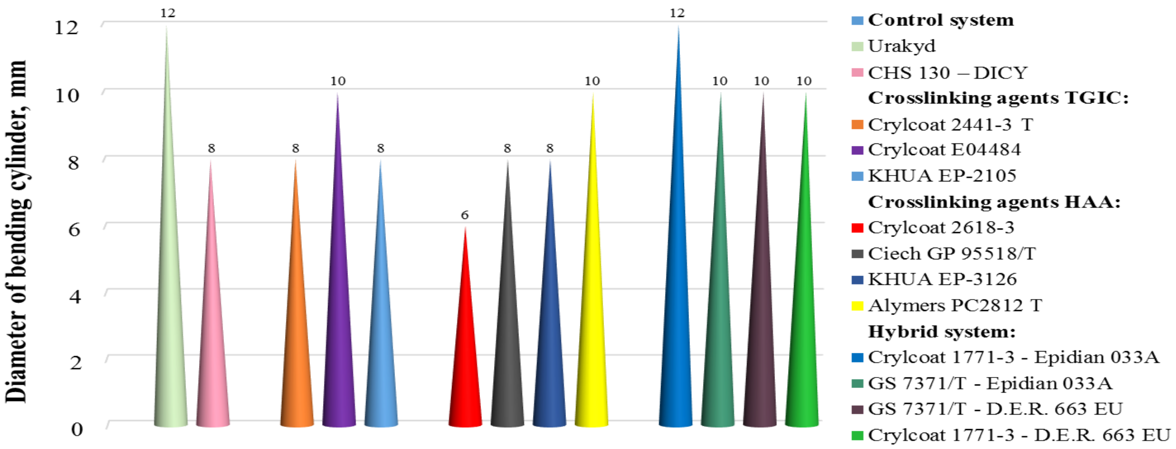

Fig. 2. Bend resistance of the powder coating

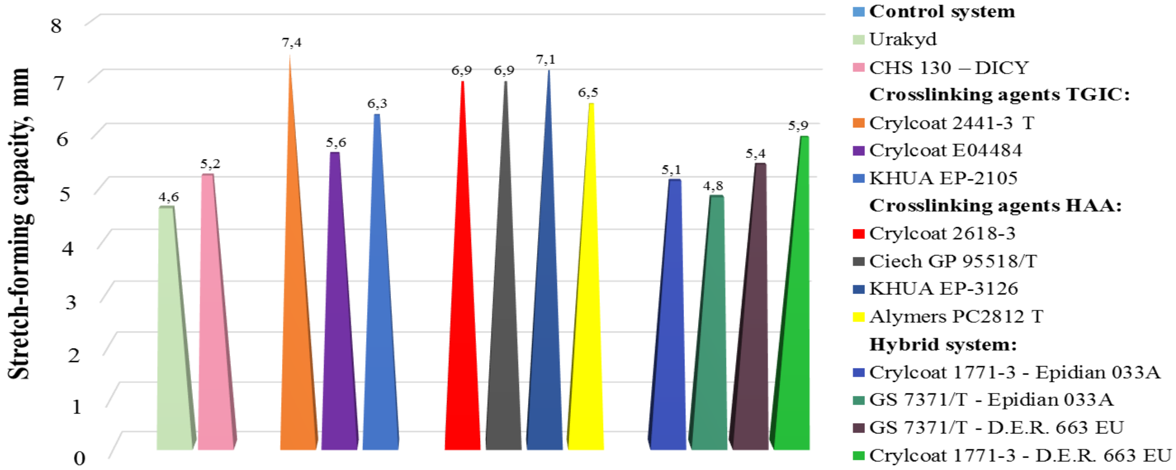

Fig. 3. Cupping test of the powder coating

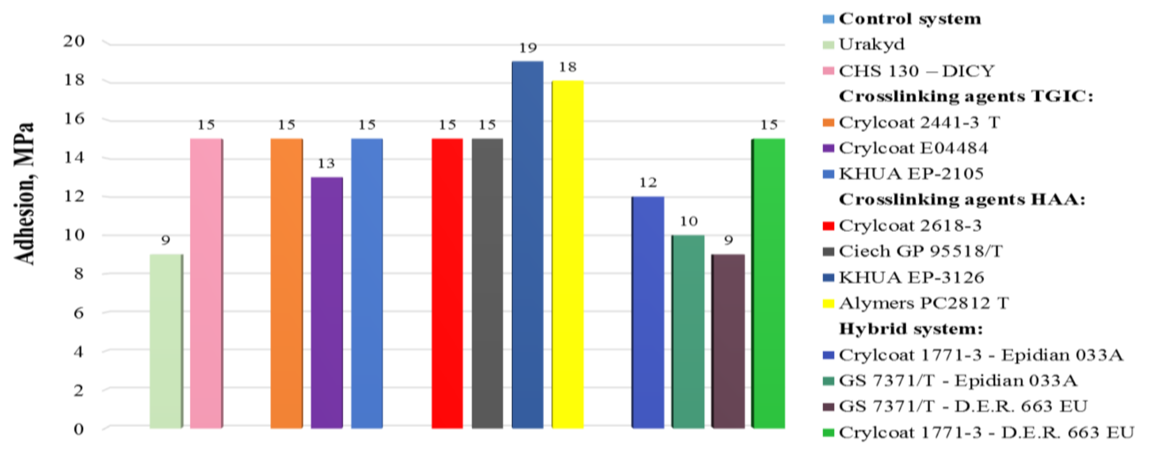

Fig. 4. Adhesion of the powder coating

Conclusions. As a result of study it has been revealed that the use of powder systems of different chemical nature provides higher physical and mechanical characteristics of coatings in comparison with traditional systems based on liquid acrylic resin, which in its turn allows to consider such systems as an alternative for protection of construction metal products and structures against the mechanical influences. At the same time, it has been shown that a change in the film former and crosslinking agent in the composition of powder systems differently influences the formation of powder coating properties depending on the type of the film former and its characteristics (viscosity, glass transition temperature) as well as the type of the crosslinking agent. The use of systems "polyester film-forming – TGIC", "polyester film-forming – HAA" provide high physical and mechanical properties of coatings without deterioration of technological properties of systems, when using film-forming with dynamic Brookfield viscosity values in the range of 3600...4200 mPa-s (at t=200 ^{o}C). In turn, the decrease of the glass transition temperature index and the increase of the resin viscosity index negatively affect the formation of the technological properties of the powder systems and, accordingly, the physical and mechanical characteristics of the coating.

The use of the "polyester-epoxy film-forming" system is less efficient compared to polyester film-forming, but the use of film-forming with low viscosity values contributes to obtaining the physical and mechanical properties of coatings at the level of the powder epoxy system.

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ЗАКОНОМІРНОСТІ ФОРМУВАННЯ ВЛАСТИВОСТЕЙ ПОРОШКОВОГО ПОКРИТТЯ В СИСТЕМІ «ПЛІВКОУТВОРЮВАЧ-ЗШИВАЮЧИЙ АГЕНТ»

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Анотація. Показано результати впливу плівкоутворювачів різного типу на формування властивостей порошкових фарб та покриттів їх основі. Порошкові фарби – один з найбільш перспективних видів лакофарбових матеріалів для промислового використання. Їх основними перевагами є: відсутність розчинників, практично безвідходна технологія нанесення покриття (ступінь утилізації порошку при застосуванні наближається до 100 %), відносна простота та економічність в процесі виробництва покриття. За результатами досліджень встановлено, що фізико-механічні та декоративні характеристики досліджуваних систем покриття суттєво змінюються залежно від виду плівкоутворювача та його основних характеристик, а також від виду зшиваючого агента. В загальному, використання порошкових систем, різної хімічної природи забезпечує вищі фізико-механічні характеристики покриттів порівняно з традиційними системами на основі рідкої акрилової смоли, що в свою чергу дає підставу розглядати такі системи як альтернативу захисту будівельних металевих виробів та конструкцій від механічних впливів. Однак, в порівнянні з епоксидною системою доцільність їх використання змінюється залежно від основних характеристик плівкоутворювача (в'язкості, температури склування) та виду зшиваючого агента. Використання систем «поліефірний плівкоутворювач – TGIC», «поліефірний плівкоутворювач – НАА» забезпечують отримання високих фізико-механічних властивостей покриттів без погіршення технологічних властивостей систем при використанні плівкоутворювачів із показниками динамічної в'язкості по Брукфільду в межах 3600…4200 мПа-с (при t = 200 ^{o}C). Зменшення показника в'язкості плівкоутворювачів призводить до погіршення технологічних властивості порошкових систем. В свою чергу, зменшення показника температури склування та підвищення показнику в'язкості плівкоутворювача, негативно впливає на формування технологічних властивостей порошкових систем і, відповідно, фізико-механічних характеристик покриття.

Ключові слова: порошкова фарба, плівкоутворювач, зшиваючий агент, покриття, адгезія, міцність на згин, міцність до дії зворотного удару, міцність на витягування.

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