Modification of epoxy powder paint using vinyl polymers

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The document presents researches on epoxy powder paint modifying approaches with polyethylene, poly(vinyl chloride) emulsion and suspension and copolymer chloride with vinyl acetate. Coatings derived from epoxy powder paint are very hard and not flexible. The goal of powder paint modification with the vinyl polymers and plasticizer dibutyl phthalate was to obtain the composition of paint that coatings are less hard and more flexible.

Scientific and technological progress of paints and lacquers industry was achieved by introducing production and usage of the new type of paint materials, called polymeric powder paints. Half century ago powder paints did not even exist yet. Liquid paints were commonly used. Powder paints were firstly used when powder resin and polymer discovered. Then it was possible to develop modern methods of production and to increase the efficiency of protection and coating quality. Nowadays a powder paints is one of the best and the most perspective assortment of anticorrosion materials [1÷3].

Powder paint is multi-component dispersion systems. They are categorized according the type of polymer or resin they contain e.g. epoxy, polyester polyvinyl, polyamide resin etc. According to predestination they are classified based on resistance to: atmospheric factors, chemical environment, anti-friction, electric insulation, for motorization, household equipment etc. Can be also specified the manner of their application, such as: fluidization, electrostatic or gas flame [4].

Generally, powder paints contain polymers and resins which are crystals, vitreous or amorphous in the solid state and are able to transfer to plastic state, which enables melting and forming protective membranes. They are divided on paints with thermoplastic polymers and thermo reactive resins. Resins used in thermo reactive composition are characterized by softening point, which can't be lower then 70°C. Those requirements are fulfilled by oligomer, which relative molecular mass is between 1500 and 3500. Experiments pointed that the epoxy powder coating resins are best, having from 2 to 6% of free epoxy groups [5]. Improvement of the properties of epoxy coatings can be by introduced polyaniline or cooper nano-particles with nano-silica [6]. Another way is to add of montmorillonite, or siloxane compounds of the immidazole rings [7].

It is important to properly wet of the powder coating of all components of a polymer or resin, while and the creation of coating and its implications for the fluidity of paint on the surface of the alloy coated product. Significant impact on the paint stability may be introduced by add-ons such as plasticizers, light and thermal stabilizers and modifiers [8 ÷10].

Recent patents inform about a few powder paints compositions, with range of their applications. It is very interesting, the way of coating production of powder paint which includes fluorine polymer [11]. Another patent describes powder composition which includes epoxy compound and cyclic acid anhydride [12]. It is also very interesting the composition of the powder paint based on semi-crystalline polyesters and a radiation-curable [13]. Another composition of the powder paint is made up of unsaturated polymer and a cross linking agent which is pre-polymer [14]. The next invention regards to thermosetting powder coating compositions containing polyester with carboxylic groups [15]. Polyester inclusive tertiare carboxylic were got from aliphatic or aromatic polyol and polycarboxylic acid [16]. Radiation-cross linked powder paint is an ester mono or policarboxyl which includes hydroxyallylamid group [17]. Antistatic powder paints consist of non-conductive, thermosetting resins [18]. Coatings from the powder paints, witch have low gloss harden radically are got by cross linking of acrylic polymers [19].

In the researches there were examined the properties of physical and mechanical parameters of composite membranes, epoxy powder paint of vinyl polymer sand and tends to indicate the possibility of their change..

Experimental part

Materials

Researches were executed with following materials: epoxy powder paints named Faproxyd white color SWW 7459-788-XXX, paints particle are spherical in shape and their dimensions do not exceed 10.0 μm, bulk density are about 0.65 g/cm^3, produce by PPG Industrial Coatings, Polifarb Cieszyn S.A., polyvinyl butyral Polioform BL-18 is acetal of polyvinyl alcohol included from 65 to 85%wt. vinylobutyral groups (vinyl acetal) and from 19 to 32%wt. vinyl alcohol groups and around 3.0%wt. vinyl acetate. It glassy temperature is 66°C, produce by Wacker Polymer Systems, polyethylene low density Polythene Dohm of melting temperature around 110 - 120°C, density around 0.916 – 0.924 g/cm^3, molecular weight 21000 – 28000, United Kingdom product, emulsion poly(vinyl chloride)

(PCW-E)68 Pmbs at number K=69.5 from Chemical Factory Synthos Dwory Sp.z.o.o. in Oświęcim, suspension poly(vinyl chloride) (PCW-E) Tarwinyl S-68, K=68 from Chemical Factory in Tarnów, copolymer of vinyl chloride vinyl acetate (CV/OV) Winicet 60/10 of K=60, product Chemical Factory in Oświęcim, plasticizer phthalate dibutyl reagent POCH in Gliwice, metal tile made of steel St3S about external dimension 60x90x0.6mm, mechanically cleaned with abrasive paper 180 and 240 and next degreased in an organic solvent (painter's naphtha, ethyl or butyl acetate), metal template from steel St3S about external dimension 60x90mm and internal fields 50x80 mm and thickness 1.0 mm.

Test's methodology

Polymers composition received by physical mixing in mortar epoxy powder paint sample and polymer or two polymers and plasticizer. Thereafter, with spatula powder polymer composition was put into the template which lies on clean steel tile surface. With a glass rod the sample surface was leveled with the surface of the template. Then the template was removed. This way, the prepared sample of powder composition was melting in a thermostat at 160 -163°C for 40 minutes. After that time, sample was taken out and slowly cooled down to room temperature. To assess the quality of the composite coatings, there were used test methods according: designation of coatings adherence (PN-80/C-81531), designation of coatings relative hardness (PN-73/C-81530), designation of coatings drawability (PN-75/C-81529), the thermo-mechanical tests along determining the softening temperature of the coatings, environmental tests involving cooking samples in boiling water for a period of 2.5 hours (PN-76/C-81521).

Test's results

Polymer composites are usually mixtures of several polymers of different properties. By mixing them there can be a material composed, that will have intermediate properties or a completely new ones, that no polymer included in its composition had and thus extend the application of polymeric materials.

Polymer composites consisting of epoxy powder paint and a variety of polymers were prepared by mixing and next melting. Obtained membranes were dispersible materials, not separating to particular layers. Table 1 shows the calculated values of Hildebrand solubility parameters for the epoxy powder paint, which main component is epoxy resin, polyethylene, poly(vinyl chloride), copolymer of vinyl chloride with vinyl acetate and polyvinyl butyral. Based on knowledge of solubility parameters there was calculated the mixing factor of composition, created with components which were mentioned polymers [9].

Table 1

Hildebrand solubility parameters values and mixing factor for the studied polymers

Types of polymer	Accepted marks	Solubility parameters $MPa^{1/2}$	Mixing factor			
			EP	PE	PVC	CV/OV
Epoxy resin	EP	22.4				
Polyethylene	PE	16.2	15.50			
Poly(vinyl chloride)	PVC	19.5	11.02	10.85		
Copolymer of vinyl chloride and vinyl acetate	CV/OV	13.4	17.95	9.10	14.20	
Polyvinyl butyral	PVB	14.6	17.00	7.02	12.90	5.80

Data presented in table 1 shows that mutual solubility of polymers is minimal. It proves that a solid two-phase colloid dispersion system could be created. In the researches there were not studied epoxy powder paints from the same polyvinyl butyral, because coating obtained from epoxy powder paint as well as polyvinyl butyral showed high hardness, low flexibility and were very fragile. It was intended to increase flexibility of epoxy coating with preparing composition with polymers and plasticizer. Tested compositions consisted of an epoxy powder paint and two or three polymers and dibuthyl phthalate. With thermo-mechanical curve of membranes samples softening point was determined. The study shows that the relative hardness coatings are decreasing with the increasing of the amount of polymer powder in the composition of the epoxy powder coating. In the case of compositions containing PVC emulsions or suspension or copolymer CV/OV coatings that show adhesion and good decoration properties, they can be obtained only if the amount of polymer does not exceed 70% by weight. Drawability tests of coatings obtained with composition of epoxy powder paint and selected polymers show it is growth, with the increasing of polymer content in the composition of the epoxy powder coating. These dependencies are shown by equation:

$$T_w = 0.45 - a \cdot c_p \qquad (1)$$
$$T_t = 0.30 + b \cdot c_p \qquad (2)$$

where T_w is the relative hardness of the coating, T_s is coating drawability in mm, c_p is the amount of polymer in the composition of epoxy powder paint in % by weight.

Constants value in the equations 1 and 2 are given in Table 2.

Table 2

Constants in equation 1 and 2 describing the change of relative hardness and drawability of coatings from epoxy powder paint compositions

Types of polymer in composition with powder paint	Types of constant	
	a	b
EP-PE	0.003	0.082
EP-PVC-E	0.005	0.004
EP-PVC-S	0.005	0.002
EP-CV/OV	0.004	0.009

The following test included preparing the powder composition of polyvinyl butyral with polymers and receipt of these coatings. It was found that good coating quality is obtained from the polyvinyl butyral composition with polyethylene used with any weight ratio. The coating quality of the polyvinyl butyral composition with other polymers can be obtained only if they do not exceed 30.0% weight. The change of relative hardness, drawability and the softening temperature of coatings obtained from these compositions are described as follows according to:

$$T_w = c + d\, c_{PVB} \qquad (3)$$
$$T_t = e - f\, c_{PVB} \qquad (4)$$
$$T_m = 90 - g\, c_{PVB} \qquad (5)$$

where T_m is the temperature of softening; c_{PVB} is the amount of polyvinyl butyral in the composition with polymer in % by weight.

Constants occurring in equations (3) ÷ (5) are given in Table 3.

Table 3

Constants in equations 3,4 and 5 describing the change in the relative hardness, drawability and softening temperature of coatings from polyvinyl butyral composition

Types of powder composition	Types of constant				
	c	d	e	f	g
PVB – PE	0.14	0.004	8.70	0.08	0.36
PVB - PVC-E	0.02	0.005	2.64	0.02	0.17
PVB - PVC-S	0.05	0.005	2.52	0.02	0.14
PVB - CV/OV	0.04	0.005	2.57	0.02	0.19

As presented in Table 3 increasing the amount of polyvinyl butyral in the composition of the causes coating hardness increasing with a simultaneous decreasing the flexibility and softening temperature. The tests carried out confirmed there were the similar properties of the epoxy coating of powder paint and polyvinyl butyral. In this situation it was decided to perform the compositions that would consist of polymer powder and a plasticizer. At first a mixture of polyvinyl butyral with vinyl polymers and phthalate dibutyl was tested. On the basis of tests it was found that the best decorative coatings and physical and mechanical properties were obtained from the mixture, which consists of 65.0% by weight vinyl polymer (PVC-E or PVC-S or copolymer CV/OV) and 35.0% by weight plasticizer DBP. After mixing polymer with plasticizer composition on figures damply powdery pulverizes was received. Then a weighed sample of this mixture was added to polyvinyl butyral. In this way the polymer composition was received that PVB was in the range of 30.0 to 70.0% by weight. It was found that in that the amount of PVB in the composition with plasticizers vinyl polymers coating properties was changing according to dependence below.

$T_w = 0.050 - 0.0007c_{PVB}$ (6)

$T_t = 11.4 - 0.08\ c_{PVB}$ (7)

$T_m = 23.0 + 0.4c_{PVB}$ (8)

It was found that the type of vinyl polymer in the composition with plasticizer and polyvinyl butyral had no effect on coating properties. In this case, the coatings show similar external appearance and physical and mechanical properties. Introducing of a plasticizer to the polymer powder composition resulted with relative reduction of hardness and increasing drawabiling and lowering the coatings softening temperature.

The following test consisted in determining the properties of coatings divided from composition of epoxy powder coating, polyvinyl butyral and vinyl polymer additive. Coatings with the best properties were obtained from the optimal composition, which consisted of 40% by weight epoxy powder paint, 10% by weight tested vinyl polymer and 50% by weight polyvinyl butyral. In this case relative hardness of coating was about 0.4, drawability 0.6 mm and melting temperature 98°C.

The last composition was mixture of epoxy powder paint, plasticized vinyl polymer (PVC-E or PVC-S or copolymer CW/OW) and polyvinyl butyral. In those mixtures vinyl polymer included 35% by weight plasticizer. The input composition consisted of a mixture of 50% by weight epoxy powder paint and 50% by weight plasticized vinyl polymer then the polyvinyl butyral was added in an amount up to 70% by weight. Then the properties of the coatings varied in accordance with following dependencies:

$T_w = 0.25 - 0.11\ c_{PVB}$ (9)

$T_t = 7.6 - 0.084\ c_{PVB}$ (10)

$T_m = 70.0 - 0.10\ c_{PVB}$ (11)

It turned out that among all the studies compositions the best physical, mechanical and decorative properties expressed by the uniformity and gloss, which is the appearance of the coating is retrieved divided from the last category of how to modify the epoxy powder paint.

Summary

Executed tests proved, it can be concluded that epoxy powder has the best miscibility with polyethylene which changes the properties of the coatings formed from this mixture most significantly. Coatings made from mixture of poly(vinyl chloride) emulsion or suspension as well as the copolymer of vinyl chloride and vinyl acetate. Similar characteristics of lower mixing ability occur in case of polyvinyl butyral in composition with poly(vinyl chloride) emulsion or suspension and copolymer vinyl chloride and vinyl acetate. Such coatings, have worse physical and mechanical characteristics. It can be up to 30% by weight of polyvinyl butyral in the vinyl polymer composition. Coatings of highest elasticity and also lowest hardness and biggest drawability are received by compositing of mixture vinyl polymer with 35%wt. plasticizer and next by the adding of a polyvinyl butyral in an amount from 30 to 70%wt. Coatings with the best decorative and physical properties were obtained with epoxy powder paint vinyl polymer and polyvinyl butyral. It was possible to boats them by introduction elasticity plasticizer. Among all the received coverings the last kind was especially glossy and uniformity.

English translation by the Author

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