Influence of modifying additives on properties of the powder coatings

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Abstract. The study deals influence of modifying additives on properties of the powder coating. The authors Using rheological and degassing modifying additives with different nature of the main active substance. It was found that the additives based on the acrylate polymer adsorbed on the silicon dioxide in the form of Byk-3900P and on the polyoxyethylene derivative of the castor oil in the form of Luvotix R400 decreasing the surface tension in the coating film, which, in its turn, contributes to the increase in the wettability of base during the melting of the powder coating, decrease the ‘orange peel’ effect during the cross-linking, reduction in pinholes on the obtained surface and improvement of mechanical characteristics of the coating. At the same time, rheological additives based on the bentonite in the form of Luvogel 4B and on the hydrophilic silicon dioxide in the form of Cab-o-sil M5 cause the increase in the surface tension in the coating film, which, in its turn, leads to the worsening of flow, appearance and mechanical characteristics of the powder coating.

1. Introduction

Powder coating is one of the most perspective materials to create a technical and economic, environmentally friendly decorative and protective coating for a wide range of building products and constructions. In the first instance, powder coatings play an esthetic role in improving the appearance of the product while ensuring high mechanical and chemical stability of the coating [1, 2].

Rapid rates of development in production of powder coatings are, in comparison to liquid paint-and-lacquer materials, evidence of their importance, high effectiveness and prospectivity [3, 4]. The increase in popularity of powder coatings can be explained by their environmental adequacy and attractiveness from the perspective of the environmental protection as well as high effectiveness related to the possibility of obtaining high quality protective and decorative coatings during the one-layer application. At the same time, it is obvious that during modern powder coating-and-lacquer materials have not exhausted all possibilities of improving pharmaceutical compositions and expanding the assortment as well as modernizing their production technology the relatively short period of their development [5].

The composition of the thermosetting powder coating contains five key components: polymer resin, hardener, pigments, fillers and functional additives [6]. In general, the polymer resin and hardener play a key role in ensuring necessary mechanical characteristics and lifespan of the powder coating. In this case, the role of functional (modifying) additives is extremely important to obtain characteristics that are often fundamentally required to meet predetermined technical specifications of the products and needs of end users.

Additives play an important role in forming properties of powder coatings and coatings based on them as they have become their integral part for several main reasons: because of control of rheological properties, surface defects as well as light and temperature stabilization of coatings. In Richard’s opinion [7], a ‘perfect’ additive for powder coatings and coatings based on them must meet the following requirements: it must be solid and in the form of the fine powder with the crystalline melting temperature Tg > 50 °C; it must not chemically react with the adhesive and hardener; it must be 100 % reactive and effective at the low level of addition.

Thus, the modern approach to the production of powder coatings provides for the improvement of
their properties using complex modifiers that help in obtaining high physical and mechanical as well as performance properties of the powder coating-and-lacquer material.

The purpose of this paper is to study the influence of modifying additives on the formation of properties of the powder coating.

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

The carboxylated polyester resin Crylcoat 2618-3 by Alnex has been used as a film-forming component. Its characteristics are listed in the Table 1. It is also necessary to use a structure-forming hardener together with the carboxylated polyester resin. In this article we have used Primid XL-552 by EMS-Griltech. As a filler the silicate in the form of metakaolin from Hlukhivtsi has been used that allows obtaining the powder coating with high physical and mechanical as well as performance characteristics according to the analysis [8, 9].

| Type of the resin | Appearance | Glance 200/600, % | Brookfield viscosity 200°C, mPa.s | Glass transition temperature, °C | Acidity (mg KOH/g) | Hardening temperature and time |
|-------------------|------------|-------------------|----------------------------------|-------------------------------|-------------------|-----------------------------|
| Crylcoat 2618-3   | Non-transparent granules | 67                 | 4000-5200                        | 60                            | 30-35             | 180°C 10min                 |

As modifying additives the additives of two various groups have been used: 1 – rheological additives; 2 – degassing additives.

The film formation and flow of thermosetting powder coatings are regulated by two key parameters, namely, surface tension and melt viscosity [10]. The surface tension is a key driver (during the set hardening regime) that causes the flow of the powder coating. The only one resistance to the flow behaviour is the viscosity index of the melted coating within the conditions of its hardness. So, the additives controlling rheological properties of the powder coating can be more precisely classified as ‘surface tension modifiers’.

As surface tension modifiers of the first group the additives of the following various nature have been used: a) – acrylate polymer adsorbed on the silicon dioxide in the form of Byk-3900P by Byk Germany; b) – polyoxyethylene derivative of the castor oil in the form of Luvotix R400 by Lehmann & Voss & Co Germany; c) – modified bentonite in the form of Luvogel 4B by Lehmann & Voss & Co Germany; d) – hydrophilic silicon dioxide in the form of Cab-o-sil M5 by Cabot.

To avoid the microcracks in the powder coatings, the release of air caught by them is required during the flow in course of their hardening. The reason is that during the cross-linking the viscosity of the powder coating increases drastically, which leads to the decrease in the release of volatiles caught by the coating film and affects the formation of physical and mechanical as well as performance properties of the material. Therefore, to obtain the high quality of the coating film it is appropriate to use degassing additives in the composition of coatings.

As degassing modifiers the additives of the following various nature have been used: a) – modified hydroxyl ketone in the form of Benzoin by Tech-Power Huangshan Ltd; b) – modified polyethylene in the form of Ceraflour 962 by Byk Germany; c) – micronized Ethylene-Bis-Stearamide in the form of Ceratan MA7019 by Munzing; d) – oxygen-containing high molecular silicon compound in the form of Powderadd 9423 by Lubrizol.

Research methods. Properties of decorative and protective powder coatings using various groups of modifying additives have been studied in the following sequence:

1. The powder coating of colour RAL 9016 has been applied on steel plates Cr3 (150x60 mm in size) using the white pigment titanium dioxide K-2190 by Kronos in its composition. The powder coating has been applied by electrostatic method according to ISO 1514:2016 using the spray gun Start 50.
2. The powder coating has hardened on sample plates in the polymerization oven at 180°C within 10 min.
3. The flow has been studied in accordance with ISO 8130-11:2019 [11] that establishes the method for determining rheological properties of the melted coating made of the thermal hardening powder on the plane inclined at a given angle to the horizontal. The principle of method is as follows: The powder coating was compressed into the tablet at a given pressure and placed on the inclined heated surface exposed to melting. Then the baking is observed during a given period of time and the drainage rate over the inclined surface is measured.
4. The impact resistance of the coating to the reverse impact has been determined in accordance with DSTU ISO 6272-2:2015 [12]. The purpose of this control is to check powder coatings for fast deformation and to evaluate their resistance to cracking and / or peeling out of the surface being coated when they are exposed to deformation due to the dropped object of a given weight with the spherical hammer head.
5. The bend strength of the coating has been determined in accordance with DSTU ISO 1519:2015 [13]. The purpose of this test is to evaluate the resistance of powder coating to cracking and (or) peeling out of the substrate (lining) by bending studied plates of the coating about the cylinder rod using the testing device equipped with a set of ball joints, each of which is linked to the cylinder rod with the relevant diameter.

3. Research results.

The composition of the powder coating has been prepared by mixing together dosed raw materials in wheel-type mixers and homogenizing the mixture (at 80...120 °C) in thermostatic screw mixers (extruders), pressing the pasty mixture out the extruder, cooling it and breaking to pieces with special mills. As a control composition the powder coating with the following ratio of raw materials has been selected: Crylcoat 2618 - 30 %; Primid XL-552 – 3.2 %; metakaolin – 20 %; TiO₂ – 16.8 %. Modifying additives have been added over 100 % of the mass of components in the control composition of the powder coating. Compositions of studied powder coatings based on the control composition using modifying additives as well as research results are shown in the Table 2, Table 3.

| Composition No | Rheological additives | Visual assessment | Flow, sm | Impact resistance, sm/kg | Bend strength |
|---------------|-----------------------|------------------|----------|-------------------------|--------------|
| 1             | BYK 3900P             | -                | +        | 3.5                     | 60           | 8            |
| 2             | Luvotix R400          | -                | +++      | 4.0                     | 80           | 8            |
| 3             | Luvogel 4B            | 0.5              | -        | 3.2                     | 50           | 8            |
| 4             | CAB-O-SIL M5          | 1.0              | +        | 3.3                     | 60           | 8            |
| 5             | -                      | 0.5              | -        | 2.7                     | 15           | 10           |
| 6             | -                      | 1.0              | -        | 2.0                     | 5            | 12           |
| 7             | -                      | 0.5              | -        | 2.9                     | 20           | 10           |
| 8             | -                      | 1.0              | -        | 2.2                     | 10           | 12           |
| 9             | 1.0                    | 0.5              | +++      | 4.5                     | 90           | 8            |
| 10            | 1.0                    | 0.5              | +++      | 3.0                     | 30           | 8            |
| 11            | 1.0                    | -                | 0.5      | 3.1                     | 40           | 8            |
| 12            | 1.0                    | 1.0              | +++      | 5.0                     | 80           | 8            |
| 13            | 1.0                    | 1.0              | +        | 2.2                     | 15           | 8            |
| 14            | 1.0                    | 1.0              | +        | 2.4                     | 20           | 8            |

*Note: - - negative, + - satisfactory, ++ - good, +++ - excellent.
Table 3. Influence of degassing additives on properties of the powder coating.

| Composition | Degassing additives | Visual assessment* | Flow, sm | Impact resistance, sm/kg | Bend strength |
|-------------|---------------------|---------------------|----------|--------------------------|--------------|
| №           | Benzoin Ceretan MA7019 Ceraflour 962 Powderadd 9423 | | | | |
| 1           | 0.3 - - - ++ | 3.5 | 60 | 8 |
| 2           | 0.6 - - - + | 4.0 | 80 | 8 |
| 3           | - 0.5 - - | - | 3.3 | 30 | 8 |
| 4           | - 1 - - | + | 3.4 | 40 | 8 |
| 5           | - - 0.5 - | - | 2.7 | 15 | 10 |
| 6           | - - 1 - | - | 2 | 5 | 12 |
| 7           | - - - 0.5 | - | 2.9 | 20 | 10 |
| 8           | - - - 1 | - | 2.2 | 10 | 12 |
| 9           | 0.3 0.5 - - +++ | 4.5 | 80 | 8 |
| 10          | 0.3 - 0.5 - +++ | 3.0 | 30 | 8 |
| 11          | 0.3 - - 0.5 ++ | 3.1 | 40 | 8 |

*Note: - - negative, + - satisfactory, ++ - good, +++ - excellent.

According to the results it has been established that rheological additives (Table 2) have a different influence on the formation of properties of the powder coating. For example, according to the visual evaluation criterion, the most effective thing is to use the additive based on the acrylate polymer adsorbed on the silicon dioxide in the form of Byk-3900P. Adding such additive in the quantity of 1% contributes to the increase in the flow index from 3.0 to 4 cm, obtaining the smooth powder coating and prevents the formation of noticeable visual defects (Figure 1). At the same time, the powder coating without the rheological additive is characterized by small pin holes and the creation of the ‘orange peel’ effect (Figure 1, b). This effect has been caused by problems resulting from local differences in the surface tension (wettability of base) of the melted powder coating film, which forces the melted film to move to the direction of the upper surface tension and leads to the formation of the ‘orange peel’ and pin holes. However, adding the mentioned additive has a positive influence on properties of the interfacial area, by that smoothing local differences in the surface tension of base and contributes to obtaining the high quality coating without any noticeable visual defects.

Figure 1. Influence of rheological additive on appearance and wettling of powder coating:
- a) with additive Byk-3900P;
- b) without additive.
It should be also noted that adding the additive in the form of Byk-3900P causes the increase in the impact resistance of the coating to the reverse impact from 50 cm/kg (control composition) to 80 cm/kg (Figure 2) and bend strength (8 mm).

Using the additive based on the polyoxyethylene derivative of the castor oil in the form of **Luvotix R400** causes the increase in the flow index from 3.0 cm to 3.2–3.3 cm but it does not ensure the high smoothness of the coating (Figure 3) where the ‘peel orange’ is seen. Adding the additive also contributes to the increase in its impact resistance to the reverse impact from 50 cm/kg (control composition) to 60 cm/kg (Figure 2) and bend strength (8 mm).

Using the additive based on the modified bentonite in the form of **Luvogel 4B** leads to the decrease in the flow index from 3.0 to 2.0 cm and worsening of smoothness of the coating with the formation of so called ‘texture coating’ (Figure 4). In this case, we can see the sharp decrease in the mechanical resistance: decrease in the impact resistance to the back impact from 50 to 5 cm/kg and flexural strength to 12 mm. The reason is that additives in the form of bentonite represent highly dispersible modified layered silicate with the high binding ability, adsorption and catalytic activity, which, accordingly, decreases the flow and wettability of powder systems and worsens the smoothness of the coating and their physical and mechanical characteristics.

Adding the additive based on the hydrophilic silicon dioxide in the form of **Cab-o-sil M5** also leads
to the decrease in the flow index from 3.0 to 2.2 cm and worsening of smoothness of the coating with the formation of so-called ‘texture coating’ (Figure 5). In this case, we can see the decrease of the impact resistance to the back impact from 50 to 10 cm/kg and flexural strength to 12 mm.

Figure 5. Visual appearance of the powder coating using Cab-o-sil M5, %: a) 0.5; b) 1.0.

The most effective thing is to use a combination of rheological additives in the form of Byk-3900P and Luvotix R400 (compositions No. 9 and No. 12 according to the Table 2) that cause the considerable decrease in the surface tension, which, in its turn, contributes to the increase in the flow from 3.0 to 5.0 cm and improvement of quality of the powder coating in comparison to the control composition. The reason is that since there are no solvents in the powder coatings, their melts have a quite high surface tension, which can affect the quality of the polymer coating. Additives that decrease the surface tension of the powder coating improve not only the flow but also the appearance of the obtained coating while preventing the defect formation.

Thus, the additives based on the acrylate polymer adsorbed on the silicon dioxide in the form of Byk-3900P and on the polyoxyethylene derivative of the castor oil in the form of Luvotix R400 used as flow enhancers allow decreasing the surface tension in the coating film, which, in its turn, contributes to the increase in the wettability of base during the melting of the powder coating, decrease in the ‘orange peel’ effect during the cross-linking, reduction in pin holes on the obtained surface and improvement of mechanical properties.

Degassing additives also have a different influence on the formation of properties (Table 2) of the powder coating depending on the nature of the main active substance. For example, according to the visual evaluation criterion, the most effective thing is to use the additive based on the modified hydroxy ketone in the form of Benzoin. Adding such additive in the quantity of 0.3 % contributes to the increase in the flow index from 3.0 cm to 3.5 cm (Table 3), decrease in the formation of visual defects (pores, voids) and obtaining the defect-free, smooth powder coating (Figure 6, b). This additive acts as a ‘solid solvent’ to keep the coating film ‘open’ for a quite long time so that air caught by the film can escape from it during the hardening. In this case, the impact resistance to the back impact increases from 50 cm/kg (control composition) to 60 cm/kg and flexural strength (8 mm). However, adding Benzoin in the quantity of 0.6 % is ineffective because this causes the considerable yellowing of the coating (Figure 6, c). The reason can be that during the hardening of the powder coating the modified hydroxy ketone can go into benzyl groups and their derivatives, which affects the change in the coating colour. Therefore, the desired content of Benzoin in powder coatings is 0.3 %.

Using the additives based on the modified polyethylene in the form of Ceraflour 962, micronized Ethylene-Bis-Stearamide in the form of Ceretan MA7019 and oxygen-containing high molecular silicon compound in the form of Powderadd 9423 do not cause the considerable decrease in the formation of visual defect (pores, voids) and obtaining the defects on the smooth powder coating (Figure 7). In this case, we can see the decrease in the impact resistance to the back impact from 50 to 5...30 cm/kg and bend strength to 10...12 mm (Table 3).

It should be also noted that the most effective way of obtaining the defect-free, smooth powder coating is using a combination of degassing additives in the form of Benzoin in the quantity of 0.3 % and Ceretan MA 7019 in the quantity of 0.5 %. Such combination contributes to the acceleration of release of air caught by the film during the hardening of the coating, which ensures high degassing.
properties in the system where no pores and voids are formed and there are no pinholes defects. It does not cause the yellowing of the obtained coating. In this case, we can see the increase in the impact resistance to the back impact from 50 to 80 cm/kg and bend strength to 8 mm.

![Visual appearance of the powder coating using Benzoin:](image)

**Figure 6.** Visual appearance of the powder coating using Benzoin:
a) control composition; b) Benzoin - 0.3 %; c) Benzoin - 0.6 %.

![Visual appearance of the powder coating using degassing additives:](image)

**Figure 7.** Visual appearance of the powder coating using degassing additives:
a) Ceraflour 962 – 0.5 %; b) Ceratan MA7019 - 0.5 %; c) Powderadd 9423 - 0.5 %.

4. Conclusions
Using rheological modifying additives has a different influence on properties of the powder coating depending on the nature of the main active substance. Additives based on the acrylate polymer adsorbed on the silicon dioxide in the form of Byk-3900P and on the polyoxyethylene derivative of the castor oil in the form of Luvotix R400 allow decreasing the surface tension in the coating film, which, in its turn,
contributes to the increase in the wettability of base during the melting of the powder coating, decrease the ‘orange peel’ effect during the cross-linking, reduction in pinholes on the obtained surface and improvement of mechanical characteristics of the coating. At the same time, rheological additives based on the bentonite in the form of Luvogl 4B and on the hydrophilic silicon dioxide in the form of Cab-o-sil M5 cause the increase in the surface tension in the coating film, which, in its turn, leads to the worsening of flow, appearance and mechanical characteristics of the powder coating.

The most effective way of obtaining the defect-free powder coating is using a combination of degassing additives based on the modified hydroxy ketone in the form of Benzoin in the quantity of 0.3 % and micronized Ethylene-Bis-Stearamide in the form of Ceretan MA 7019 in the quantity of 0.5 %. Such combination contributes to the acceleration of release of air caught by the film during the hardening of the coating, which ensures high degassing properties in the system where no pores and voids are formed and there are no pinholes defects. It does not cause the yellowing of the obtained coating. At the same time, adding the mentioned degassing additives as well as additives based on the modified polyethylene in the form of Ceraflour 962 and oxygen-containing high molecular silicon compound in the form of Powderadd 9423 separately does not cause the considerable decrease in the formation of noticeable visual defects (pores, voids) and obtaining the defect-free smooth powder coating.

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