Coatings with controlled degree of hydrophobicity based on powder polymer coatings

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Abstract. The coatings with controlled degree of hydrophobicity based on epoxy-polyester powder compositions on an aluminum surface were obtained. The study of changes in surface properties (contact angle and surface energy) and the physico-mechanical properties of the coatings, depending on the concentration of the fluorine additive, was carried out. Modification of the polymer powder composition with a fluorine additive leads to a sharp increase in the degree of hydrophobicity from hydrophobic to the formation of a superhydrophobic coating) and the saving of high mechanical properties of the coating obtained on them.

1. Introduction

Currently, due to strict environmental regulations, paint materials and coatings based on them are subject to stringent requirements. Therefore, an important task now is to replace organically soluble paints and varnishes with environmentally friendly materials based on polymers (oligomers) in a finely dispersed state, i.e. in the form of a powder [1,2]. Powder coatings quickly began to gain popularity both among industrialists and environmentalists. Being absolutely solvent-free, the most environmentally friendly paint and varnish products were became. Their obvious environmental, economic and functional advantages over liquid paints have allowed powder coating technology to be widely used in industry. As result, powder coatings have gained their place in the paint and varnish market.

Unlike other polymeric materials, paint coatings, including those obtained from powder polymer compositions, are thin polymer films adhesively bonded to the substrate. In this regard, their operational characteristics are essentially influenced by surface properties at the phase boundary, the improvement of which is one of the important scientific and technical problems [3].

Giving the paint coatings hydrophobic properties is an important scientific and technical task. It can significantly reduce the rate of penetration of moisture and water-soluble corrosive agents to the substrate, reduce dust and dirt retention, facilitate surface cleaning and increase their service life. With hydrophobization of coatings, it is possible to create environmentally friendly materials for new-generation anti-fouling coatings in shipbuilding, as well as anti-graffiti [4,5].

This problem being still very relevant is solved in practical terms in the following ways:

a) modification (processing) of the surface of the polymer coating;
b) the use of non-polar film formers;
c) physical and chemical modification of the polymer itself.
In all the methods presented above, the most important and necessary condition for coatings is the low surface energy that fluorocarbon polymers, polyolefins (polyethylene, polypropylene, paraffin), organosilicon polymers and oligomers have (less than 30 mJ / m$^2$) [6].

The production of highly hydrophobic coatings, the contact angle of which with water exceeds 120°, is of the greatest scientific and practical interest. Superhydrophobic coatings characterized by a very high contact angle (> 150°) can be distinguished as a separate group. The angle of inclination of the surface to the horizon at which a drop of water slides off the coating is negligible. To obtain superhydrophobic materials with a contact angle greater than 150°, it is necessary to use the combined effect of surface roughness and chemical structure. Superhydrophobic state can be achieved precisely by selection of surface texture [7,8].

Significant opportunities for obtaining water-repellent coatings are provided by the principle of using stratified compositions of the solution or emulsion type. In this case, during the formation of coatings, the system is separated in layers as a result of the components incompatibility or crystallization of one of them. The top layer must contain a low-energy component of the coating [7]. One promising and technologically simple way to obtain hydrophobic coatings is the modification of the film former with hydrophobic additives. Using special hydrophobic nanoparticles, in addition to giving the LPC surface a low-energy state, can also provide multimodal roughness (at the nano- and micro-levels), which results in formation of superhydrophobic coatings [9-12].

To date, most studies in the field of producing hydrophobic organic coatings relate to liquid paints and varnishes (organically soluble or water-dispersible) [13,14,15]. However, there is practically no data on the production of hydrophobic coatings possessing, in particular, highly hydrophobic and superhydrophobic properties and based on powder polymer compositions. In connection with the foregoing, it is relevant to develop coatings with various degrees of hydrophobicity (from hydrophobic, highly hydrophobic to superhydrophobic ones) based on powder polymer binders.

2. The experimental part

2.1. Materials and methods

As a polymer base for coatings with different degrees of hydrophobicity, epoxy-polyester powder paint (Ekolon, St. Petersburg, Russia) was used. To modify the surface properties of the coatings, a fluorine additive in the form of a fluoroplastic powder (PTFE) with a particle size of up to 5 μm was used. Powder compositions for formation of hydrophobic coatings were prepared by mixing the base with fluoroplastic according to the procedure described in [16]. Then, the obtained powder composition was applied electrostatically to an aluminum plate and, after curing at 190°C for 15 min, coatings 80–100 μm thick were formed. Subsequently, the resulting coatings were used to evaluate the physico-mechanical and de-icing properties.

Impact strength of coatings was determined in accordance with ISO 6272 on a U-2 equipment. The adhesion was determined by the method of lattice notch in accordance with ISO 2409. Tests for determining the tensile strength of the coatings were carried out in accordance with ISO 1520 on the device "Ericksen press". Pencil hardness was determined in accordance with ISO 15184-1998.

To analyze the roughness of coatings, a digital surface profilometer ELCOMETER 224 was used. The contact angle was determined on a DSA4 instrument (Kruss, Germany). The estimation of the contact angle was determined by the method of a sessile drop. The essence of the method is to apply a drop of water to the test coating, onto which light is incident, with following direct measure the angle using a camera.
2.2. Results and discussions

The introduction of 0.5 wt.% PTFE into the epoxy-powder composition leads to a sharp increase in the contact angle with water from 73° to 133°, that corresponds to the highly hydrophobic state of the material (Figure 1). With a further increase in the concentration of PTFE up to 2.0 wt.% the contact angle with water reaches 163° (superhydrophobic state).

![Figure 1](image)

**Figure 1.** Effect of the PTFE concentration on the water contact angle and surface energy of coatings based on epoxy-polyester powder paint

Apparently, upon mixing, the PTFE is adsorbed on the surface of the particles of the epoxy-polyester powder composition. Due to the adsorbed PTFE layer, the particles of the powder composition migrate to the surface layers and, therefore, form a hydrophobic rough surface [17]. At the same time, the layer of PTFE particles forms on the surface of the coating. The reason for such high contact angles of the coatings filled with PTFE is not only surface chemistry, but also the formation of a certain structure. In this regard, the surface roughness of the coatings was studied using a special digital profilometer. An increase of the concentration of PTFE in the epoxy-polyester powder composition leads to enhancement of the surface roughness (Table 1) of the resulting coatings and, as a result, the value of the contact angle with water rises (Figure 1).

The universal characteristic of a surface is surface energy, which is the result of uncompensated cohesion energy at the solid/air interface. Based on the values of the wetting contact angles of coatings with water and hexadecane, using the component theory of surface energy, the surface energy of hydrophobic coatings was calculated using the extended Fawkes equation [18].

A significant decrease in surface energy is observed with the introduction of PTFE into the epoxy-polyester powder composition, that correlates with the obtained values of the contact angle with water for the studied coatings. Thus, the surface energy decreases from 33 mJ/m² for an unmodified coating to 14 mJ/m² for the coating containing 2 wt.% PTFE.

The study of the physico-mechanical properties of coatings showed that the introduction of PTFE up to 2.0 wt.% has virtually no effect on changes in the mechanical properties of coatings and remains at a high level (as with coatings obtained from unmodified epoxy-polyester powder paint) (see Table 1). Thus, based on studies of the surface and physico-mechanical properties of coatings modified with PTFE, one can assume the following:
- The surface of the epoxy-polyester coating is enriched in PTFE, since there is a sharp decrease in surface energy and an increase in the contact angle of coatings when small PTFE additives are introduced;
- On the contrary, the interface between the coatings and the substrate is depleted in PTFE. This conclusion was made due to the preservation of the high physical and mechanical properties of the coatings, especially the adhesion of the coatings to the substrate. Thus, the physico-mechanical properties of the coatings are determined by the properties of the initial film-forming material.

Table 1. The effect of PTFE concentration on the physico-mechanical properties of epoxy-polyester coatings.

| wt.% PTFE in powder coating | Strength on impact forward / reverse (cm) | Tensile strength (mm) | Adhesion, (ball) | Hardness | Roughness, (µm) |
|-----------------------------|------------------------------------------|-----------------------|-----------------|----------|-----------------|
| 0                           | 100/100                                  | 8                     | 1               | 2H       | -               |
| 0.5                         | 100/100                                  | 8                     | 1               | 3H       | 1.7             |
| 1                           | 100/100                                  | 7.5                   | 1               | 2H       | 2.3             |
| 1.5                         | 100/100                                  | 8                     | 1               | 2H       | 4.3             |
| 2.0                         | 100/100                                  | 7                     | 1               | 2H       | 9.8             |

3. Conclusion
In the present work, the coatings with an adjustable degree of hydrophobicity (from hydrophobic to superhydrophobic) were obtained by introducing small additives of an organofluorine into an epoxy-polyester powder composition.

It has been established, that due to a simple technological method of introducing PTFE into epoxy-polyester powder paint and variation of its concentration (from 0.5 to 2 wt.%), it is possible to control roughness and to obtain coatings with contact angles with water being characteristic of hydrophobic, highly hydrophobic and superhydrophobic surface.

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