Features of nanocomposite powder paints spreading with the addition of aluminum oxide nanofibers

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Abstract. The paper studies the effect of violation of the spreading of powder paints when they are compounded with nanofibers of aluminum oxide. It is shown that with the addition of small fractions of aluminum oxide nanofibers equal to 0.05 wt%, the grains of the powder paint do not have time to wet each other, the crosslinking of the coating structure occurs up to this point, which is fixed by a characteristic granular texture. The paper also illustrates the features of the distribution of nanofibers of aluminum oxide in the coating. The increase in cohesion energy leads to a natural increase in the surface tension in the paint, which we observe in the form of the characteristic morphology of the coating. Investigation of coatings of a reference powder paint and a modified addition of aluminum oxide nanofibers were carried out using an optical microscope. Separately, the morphology of the resin was investigated by scanning electron microscopy. Increasing the proportion of the flow agent based on acrylic compounds in the polyester resin from 0.8 to 1.8 wt% solves this problem, while the strengthening effect of nanofibers of alumina in the paint is retained.

1. Introduction

Today, powder paints based on polyester resins are used as protective coatings for metals [1]. The main functions of the coating are anti-corrosion protection; the aesthetic factor of painting can be attributed to the second plan. To avoid damage to the integrity of the coating, special components are often added to the powder paint to improve the physical and mechanical properties of the polymer coating.

The main approach to improving the physical and mechanical properties is composite solutions. In a number of works, protective powder coatings have been implemented containing: SiO₂, TiO₂, Al₂O₃ nanoparticles [2], carbon nanotubes [3], graphene [4, 5], layered aluminosilicates [6, 7], plant fibers, for example, bamboo, jute, etc. [8]. The most effective additives are carbon nanotubes and graphene, due to their outstanding physical and mechanical properties, but their use is associated with difficulties in dispersion and black color of additives, which is unacceptable for paints due to the effect of the additive on the tone of the coating.

Strengthening of polymer coatings occurs by the mechanism of increasing cohesion energy, it turns out that the surface tension of the paint during its spreading and curing also increases. This work is
devoted to the consideration of this effect, which is important for the operation of nanocomposite polymer coatings.

2. Synthesis
The base of the powder paint was NH6586 resin manufactured by «Kinte», hardened by Primid crosslinker. The introduction of nanofibers into the resin from solution, followed by drying of the solvent always leads to difficulties associated with the removal of the solvent from the composite. In this work, the additive was introduced by the standard industrial method of twin-screw extrusion. The resin granules and the addition of aluminum oxide nanofibers were mechanically mixed with each other and placed into the receiving hopper of a twin-screw extruder, which was heated to the softening temperature of the resin. After the extruder, the mixture was poured onto counter-rotating rollers, which formed a belt from the softened resin and fed onto a conveyor. On the conveyor, the belt cooled down, after which it broke into small chips. To begin with, nanofibers of aluminum oxide were mixed into a pure resin, forming a masterbatch of nanofibers in resin with a mass fraction of 5%. Then the masterbatch was added to the paint formulation and mixed with resin, hardener, filler and pigments according to the manufacturing regulations. 1% masterbatch was added to the resin for each sample, which corresponds to 0.05 wt% of nanofibers of alumina by analogy with our previous works [9], in order to obtain the concentration of nanofibers in the resin up to the percolation threshold. The additive is calculated on the basis of the weight of the resin. it is distributed in the resin and increases its cohesion energy.

To test the properties and study the morphology, a nanocomposite powder paint and a reference powder paint without the addition of aluminum oxide nanofibers were applied to steel plates 0.6 mm thick and then annealed at a temperature of 200 °C to hardened it.

3. Results and discussion
The obtained coatings were tested for their physical and mechanical properties according to the set of methods set forth in table 1. The study of the morphology of coatings with the reference powder paint and a modified addition of aluminum oxide nanofibers was carried out using an optical and electron microscope.

In the images (figure 1a, 1b) optical microscopy shows that the coating on the reference conformally covers the surface so that the rolling texture of the substrate is manifested. On the modified sample, the rolling texture does not appear; in addition, the texture of the powder paint grains is preserved in the coating texture, which is explained by the low flow ability of the modified paint compared to the reference. It is obvious that the roughness of the modified coating is due to the revealed grain texture. Visually noticeable roughness is associated with the fact that there are areas of partially jointed and unjointed granular coating.

Figure 1. Optical microscopy of the coating surface. (a) - reference (b) – modified.
The grain boundary in the coating texture is a groove (figure 1b). Mutual diffusion of paint grains did not have time to pass due to the fact that the material was crosslinked before spreading and leveling by cohesive and surface forces.

The spreadability of coatings is provided by various acrylate additives in polyester resin, do they increase the mobility of polymer chains and coatings providing uniform coverage of the substrate. Usually, the industrial additive LA-88 is used in powder paints, as a rule, it is added about 0.8%, but in nanocomposite paint its amount should be increased. Various amounts of flow agent were added to the nanocomposite paint (table 1) to provide the desired finish. In total, four samples were made in addition to the reference one.

### Table 1. Results of mechanical tests.

| Name, Test method | Reference | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
|------------------|-----------|-----------|-----------|-----------|-----------|
| Portion of LA-88, wt% | 0.8 | 1 | 1.5 | 1.8 | 3 |
| Thickness, μm | 70-80 | 60-80 | 85-94 | 70-80 | 60-80 |
| Gloss, angle 60º (ISO 2813) | 83.4 | 65.5 | 83.1 | 81.3 | 65.3 |
| Strength, kg·cm, direct impact | 60 | 10 | 50 | 60 | 65 |
| Strength, kg·cm, reverse impact | 20 | 0 | 20 | 50 | 30 |
| Flexural elasticity, mm | 3 | 6 | 2 | 2 | 3 |

A slight increase in the proportion of the flow agent in Sample 1 did not change the effect of aluminum oxide nanofibers on the surface tension of the paint during its spreading. As a result, the mechanical characteristics have deteriorated significantly. However, with an increase in the proportion of the flow agent, the strength of the coating increases and, with a flow agent in the paint of 1.8%, it reaches its maximum values in the case of reverse impact, which indirectly characterizes the cohesion energy of the coating. A further increase in the proportion of the flow agent leads to delamination of the paint and the nanostructured additive. Although bundles of aluminum oxide nanofibers on the paint surface increase the strength of the coating upon direct impact, the cohesion energy of the coating decreases.

The coatings were examined by optical microscopy (figure 2). It is clear that the lack of a flow agent leads to the formation of a rather rough and rough surface, we observe this both in the original formulation (figure 1a) and with the addition of 1% flow agent (figure 2a). Comparing the coatings (figure 2b, c) with 1.5 and 1.8% flow agent, it can be seen that in the first case, we still have roughness defects, and in the second - no longer - a smooth, even surface. It is noteworthy that an excess of the flow agent (figure 2d) led to the delamination of the nanocomposite, as a result of which the bundles of aluminum oxide nanofibers coated with paint appeared on the surface, while the main layer of paint spread over the substrate. Finally, optical microscopy indirectly indicates a uniform distribution of the additive of nanofibers of aluminum oxide.
Figure 2. Optical microscopy of nanocomposite powder paints with different proportions of flow agent. a) 1% LA-88; b) 1.5% LA-88; c) 1.8% LA-88 and d) 3% LA-88.

The SEM method was used to study masterbatch in resin of alumina nanofibers functionalized with epoxy (figure 3a) groups. Alumina nanofibers in bundles are uniformly distributed over the polyester resin matrix. The bundles of nanofibers organically merge with the resin material, slightly distinguishing themselves in contrast; their size, on average, does not exceed 5 μm in diameter. The length of the beams is difficult to estimate due to the fact that it is difficult to reliably determine whether the acquisition plane on the SEM is parallel to the plane in which the beam lies.
Figure 3. Scanning electron microscopy, (a) a masterbatch with the addition of epoxy-functionalized alumina nanofibers, (b) a semi-product powder paint chips with the addition of epoxy functionalized alumina nanofibers, (c) elemental mapping along the line.

The low dispersion of the additive in the masterbatch is associated with insufficient forces created by internal friction during the distribution of nanofibers in the resin by the method of twin-screw extrusion. Nevertheless, we do not find such objects when studying the morphology of paints by the SEM method (figure 3b).

Hence, we conclude that the second extrusion and the paint filler (whose particles, presumably, play the role of particles that additionally exfoliate the beams) make it possible to distribute the nanofibers more dispersedly. Here, of course, it can be assumed that nanofibers do not get into the paint at all, but their addition definitely leads to hardening of the protective coloring coating. The presence of aluminum on the elemental mapping (figure 3c) indicates that it was the nanofibers of aluminum oxide that got into the paint, since there are no aluminum-containing fillers in its formulation.
4. Conclusion
In conclusion, it should be noted that the second extrusion and the paint filler make it possible to distribute nanofibers from the masterbatch with a higher degree of dispersion.

It is shown that with the addition of small fractions of aluminum oxide nanofibers equal to 0.05 wt%, the grains of the powder paint do not have time to wet each other, the crosslinking of the coating structure occurs up to this point, which is fixed by a characteristic granular texture. Increasing the proportion of the spreading agent based on acrylic compounds in the polyester resin from 0.8 to 1.8 wt% solves this problem, while the strengthening effect of nanofibers of alumina in the paint is retained.

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