

Performance Characteristics of Styrene-Acrylic Polymer Compositions and Coatings Filled with Dispersive Components



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Abstract The object of the study is kaolin activated in the vortex layer apparatus, which is used as a filler for styrene-acrylic paint coatings. A comparative analysis of the performance characteristics of coatings filled with initial and activated kaolins was performed. Dispersion analysis was chosen as the research method, which allowed the authors to establish that the processing of the filler in the vortex layer apparatus caused an increase in its dispersion to 6 microns. In filled paint coatings, changes in the indicators of washability, water/moisture absorption, adhesive strength, as well as resistance to aggressive media, including model ones simulating the process of biological corrosion, were determined. Coatings and the condition of their surfaces after exposure to liquid media were fixed by the CIELab method by changing the color characteristics. It was found that filling with activated kaolin provides an increase in the level of performance characteristics of coatings – washability by 3.5 times, water absorption by 2.5 times and adhesive strength by 1.5 times, as well as resistance to aggressive media.

Keywords Styrene-acrylic copolymer · Coatings · Vortex layer apparatus · Activation

1 Introduction

Styrene-acrylic paint coatings (PC) are one of the most common materials for protecting building materials, structures from external factors and corrosion [1–3]. The level of protective characteristics of coatings is largely determined by both the properties of the polymer matrix of the composition and its filling [4–6].

It is known [7–9] that one of the most common fillers of PWM is kaolin, which serves as a substitute for an expensive pigment—titanium dioxide [7, 10, 11] and contributes to the uniform distribution of dispersed mineral particles of other components of the composition [7, 12]. However, along with providing the above functions,

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kaolin filling makes it possible to reduce the level of protective characteristics of coatings. In this regard, it is urgent to find a solution for leveling the negative effect of the filler-kaolin on the properties of polymer coatings.

The protective characteristics of coatings are largely determined by intermolecular interactions between mineral components and the polymer matrix [13–15], an increase in the level of which can be provided by the activation of the filler. Among the popular activation methods, dispersion in various apparatuses is noted [16, 17], however, the most effective should include processing in a vortex layer apparatus [18–21].

Thus, the aim of the article is to study the effect of kaolin activation in the vortex layer apparatus on the properties of styrene-acrylic polymer paint and varnish protective coatings.

2 Methods

2.1 Obtaining Filler and Paint Composition

Activated kaolin was obtained in a vortex layer apparatus (ABC) Vortex297 (Fig. 1). The filler was loaded into a sealed container of the apparatus together with grinding bodies (cylindrical ferromagnetic particles with a diameter of 2 mm) and dispersed for 5 min.

The preparation of the paint composition was carried out on a dissolver according to the method [22, 23], consisting of the following stages:

- pre-mixing—distilled water and functional additives were added to the dry components with the specified ratios;

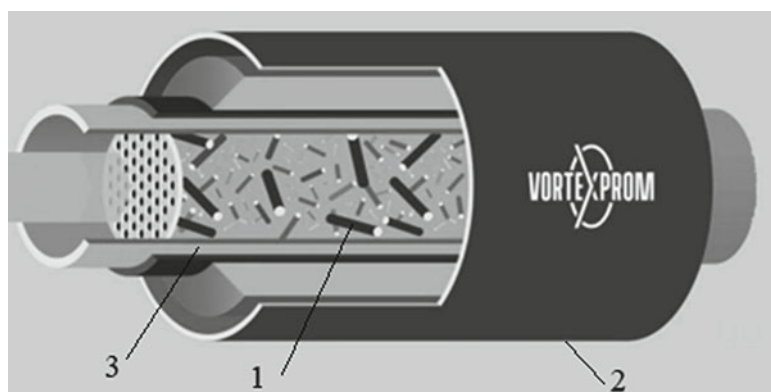


Fig. 1 Reactor of the vortex layer apparatus Vortex297: 1—ferromagnetic grinding bodies; 2—the body of the device; 3—sealed container

- preparation of pigment paste—the resulting mixture was placed in a dissolver and stirred at a speed of $n = 2000$ rpm for 30 min.;
- preparation of the composition—pigment paste was mixed with styrene-acrylic film-forming agent in a ratio of 1:0.5 (pigment paste: film-forming agent) and mixed (~30 min.) until a homogeneous lump containing no aggregates and air bubbles is obtained.

An aqueous dispersion of the homacryl 101 M brand (Homa Company) was used as a styrene-acrylic copolymer.

2.2 Preparation of Paint Coatings Samples for Testing

Free films were obtained by applying a paint composition to a fluoroplast substrate (the time of coating formation is up to 7 days at 20 ± 2 °C). The formation was controlled by changing the state of the surface to “aftertack”. Ready-made free films were used in determining the moisture absorption and action of the model medium.

To determine the values of the indicators of washability and water absorption of paint coatings, a composition was applied to a preweighed fat-free glass plate until it was completely covered and dried for 24 h at a temperature of 20 ± 2 °C.

Cement-sand samples (CSS) were cubes with dimensions of $10 \times 10 \times 10$ cm. The material of the samples is M400 grade cement, sand up to 1.5 mm in size, water. Samples were obtained by simultaneously mixing these materials in a water-cement ratio of 0.32, and pouring the resulting mixture into metal molds lubricated with a separating liquid (oil). The process of hardening the samples was completed in 7 days, after which they were removed from the mold.

Determination of water absorption and resistance to aggressive media was carried out on glass plates with paint and varnish coatings applied to their surfaces. The composition was applied to the plate until it was completely covered and then dried for 7 days.

2.3 Determination of the Characteristics of the Filler and Protective Coatings

The dispersion of the kaolin activated in the vortex layer apparatus was determined using the HORIBA LA-950 device, the principle of operation of which is based on scattering and detection of reflected/refracted laser light, red and blue spectra (650 and 405 nm), in accordance with ISO 13320-1.

One of the main protective characteristics of paint coatings are the following indicators: washability, resistance to aggressive media, water and moisture absorption.

The washability (X) of paint coatings was determined as follows. The painted glass plate was fixed in a holder and a three-row brush with natural bristles 11 ± 2 mm long, including a stopwatch, was driven in a circular motion (over the plate area). At the same time with the movement of the brush, 25 cm^3 of water was supplied to the upper part of the plate from the burette for 30 s. The flushing water was collected in a pre-weighed bowl located under the plate. After 30 s, the brush was stopped and washed with small portions of water until the paint coating particles were completely removed. The washing water was collected in the same cup and evaporated in a thermal shock to a constant mass. Then the bowl was cooled to room temperature and weighed again.

The washability value (g/m^2) of the paint coating was determined by the formula (1):

$$X = \frac{m - m_0}{S}, \quad (1)$$

m – the mass of the bowl, g;

m_0 – the mass of the bowl after drying, g;

S – the surface area of the coating, m^2 .

The arithmetic mean of three parallel definitions was taken as the test result, the absolute discrepancy between which did not exceed the permissible discrepancy equal to 0.3 g/m^2 .

Water absorption (W_p) of coatings was carried out on glass painted plates immersed in water for 24 h.

A glass plate with a cured coating was weighed and placed in a bath filled with distilled water at a temperature of 20 ± 2 °C. Air bubbles that appeared on the coating after the sample was immersed in water were removed with a soft brush. After 24 h after immersion, the plate was removed from the water, dried with filter paper, weighed and water absorption (%) was calculated according to the formula (2):

$$W_{\Pi} = \frac{m_2 - m_1}{m_1 - m_0} \cdot 100\% \quad (2)$$

m_0 – weight of a clean plate, g;

m_1 – weight of the coated plate, g;

m_2 – weight of the coated plate after the experiment, g.

Moisture absorption (W_{pl}) of coatings was determined on free films. The free films of the composition were immersed in a pre-weighed beaker with a tightly closed lid and the mass (film + cup) was determined. Moreover, the free films were placed in a desiccator, in which the relative humidity of $95 \pm 2\%$ was constantly maintained, and kept in it for 24 h. Then the samples were taken out and weighed in a tightly closed cup. The moisture absorption value (%) was determined by the formula (3):

$$W_{\Pi} = \frac{m_3 - m_2}{m_2 - m_1} \cdot 100\% \quad (3)$$

m_1 – empty cup weight, g;

m_2 – weight of a cup with a film, g;

m_3 – the mass of the cup with the film after the test, g.

The adhesive strength of paint coatings to the cement-sand surface was determined on the PSO-10MG4S adhesive meter device. Paint compositions were applied to the pre-cleaned surfaces until they were completely covered, which were further dried for 24 h. A 50×50 mm steel plate with a ball shank, an adhesive consisting of ED-20 epoxy resin (10 wt. h.) and a diethylenetriamine hardener (1 wt. h.) was glued to the formed coating. After curing of the adhesive layer, the shank was fixed in the fork grip of the adhesive meter and then a force was applied using the handle, the vector of which is directed perpendicular to the coated surface. When the arm is loaded, the strain gauge converter of the device generates an electrical signal that varies in proportion to the applied load, which is registered by the electronic unit and converted into force. The adhesion strength was calculated as the ratio of the force expended on the separation of the steel plate to its area.

The determination of changes in the quality indicators of coatings was carried out on free films, and tests of their resistance to aggressive media were carried out in acidic, alkaline and neutral media, which are—3% sulfuric acid solution; 0.1n sodium hydroxide solution and distilled water.

The presence of possible microcracks and defects on the surface of paint coatings before and after their exposure in aggressive environments was determined using a Levenhuk DTX90 digital microscope (magnification $\times 280$).

The color characteristics of the free films were changed in accordance with GOST 52,490–2005. In the graphical light model, the “lightness” is given by the L coordinate, and the chromatic component of the color is given by two Cartesian coordinates a and b (Fig. 2).

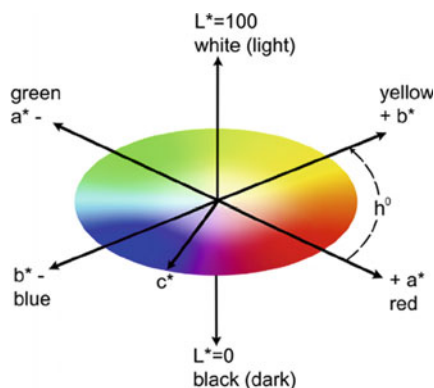


Fig. 2 Graphical representation of the lab color model

Processing of the results obtained by measuring the coordinate data of the comparison samples and the tested paint coatings, and subsequent calculations of the parameters of the difference in their color characteristics, was carried out according to the formulae (4–7):

– total color difference:

$$\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (4)$$

$$\Delta L^* = L_T^* - L_R^* \quad (5)$$

$$\Delta a^* = a_T^* - a_R^* \quad (6)$$

$$\Delta b^* = b_T^* - b_R^* \quad (7)$$

где:

$\Delta L^*_T, \Delta a^*_T, \Delta b^*_T$ – color coordinates of the test sample;

$\Delta L^*_R, \Delta a^*_R, \Delta b^*_R$ – color coordinates of the comparison sample.

$\Delta L^*, \Delta a^*, \Delta b^*$ – the difference between the color coordinates of the test sample and the comparison sample.

2.4 Testing in Model Media

Determination of the biostability of paint coating samples was carried out in a laboratory kinetic plant [24]. The tests were carried out for 7 days at a medium temperature of 40 ± 2 °C, which, according to the Van't Hoff rule, is equivalent to 28 days at 20 ± 2 °C with automatic regulation of the main parameters of the medium – temperature and pH (3.45).

The laboratory plant consists of a test tank in which the test samples immersed in the model medium are installed, a make-up tank, a drain tank, as well as a measuring tank for determining the pH of the model medium and pH electrode calibration, an electronic control unit that performs the functions of measuring the pH, temperature of the model medium and maintaining them at a given level.

A mixture of carboxylic acids was used as a model medium: oxalic, tartaric, malic, lactic, citric and acetic acids, the choice of which is due to their presence in the metabolites of bacteria isolated in public and residential premises [25, 26].

3 Results and Discussion

It is known [13, 14] that filling with a highly dispersed filler causes not only an increase in contact between the filler particles and the film-forming agent, but also ensures a uniform distribution of dispersed components in the volume of the polymer coating. According to the results of the dispersion analysis, it was found that its processing in the vortex layer apparatus contributes to an increase in the degree of dispersion of the filler to 6 microns (Fig. 4), compared with the initial kaolin (Fig. 3).

The high dispersion of activated kaolin contributes to a more equal distribution of components in the coating volume, which leads to an increase in operational characteristics (Table 1). It was found that the washability of paint coatings, when filled with activated kaolin, decreases by 3.5 times, and water absorption by more than 2.5 times. It should also be noted that the moisture absorption index decreased to 4.4%.

The analysis of the adhesive strength results showed that the filling with activated kaolin provides a high level of adhesion of the protective coating with a cement-sand substrate—3.22 MPa, compared with an inactive filler.

The high level of adhesive strength can also be explained by an increase in the contact area of the PC with the protected surface due to the high dispersion of the

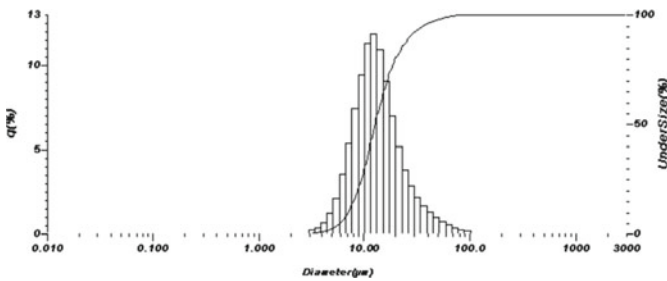


Fig. 3 Dispersed particle distribution of the initial kaolin

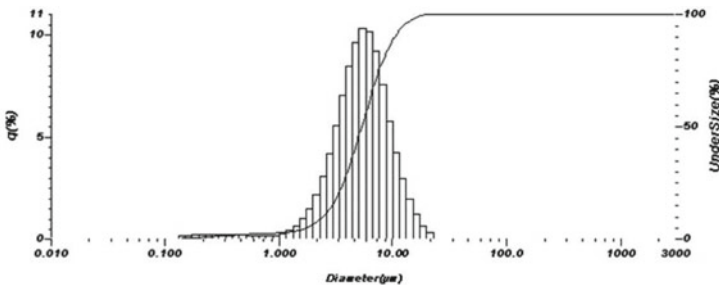
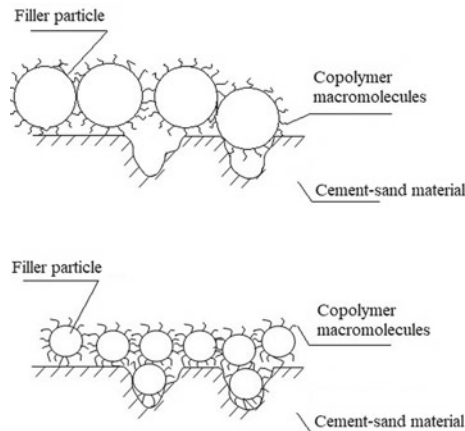


Fig. 4 Dispersed distribution of kaolin particles activated in the vortex layer apparatus

Table 1 Results of determining the performance characteristics of paint coatings

Parameters	The parameter values of the filled paint coatings	
	Initial kaolin	Activated kaolin
Washability, g/m ²	17,8	4,8
Water sorption, %	15,1	5,2
Moisture sorption, %	5	4,4
Adhesion strength, MPa	2,01	3,22

**Fig. 5** Schematic representation of the effect of high dispersion of activated kaolin on increasing the contact area between the substrate and the composition

filler—activated kaolin, which is schematically shown in Fig. 5 and confirmed by the increased area of separation of the “mushroom” from the surface of the CSS (Fig. 6).

Resistance to aggressive media is a parameter that allows judging the durability of the paint coatings. The change in the color characteristics of the PC surface before and after their exposure, as well as the state of the appearance of the coating surface (Fig. 7) were selected as the determined and controlled parameters.

It was found that filling the composition with the initial kaolin causes partial destruction of the film under the influence of an alkaline medium and the removal of its upper (non-exposed) parts (Fig. 8a).

The introduction of activated kaolin into styrene-acrylic coatings increases their resistance to aggressive media and the absence of defects and destruction on the surface of the PCs under the action of alkaline and neutral media (Fig. 8b).

In the comparative analysis of the initial color characteristics of coatings (Table 2) it was found that the kaolin filling has a negligible effect on the value of the chromaticity coordinates (L, a, b) when they are compared with each other.

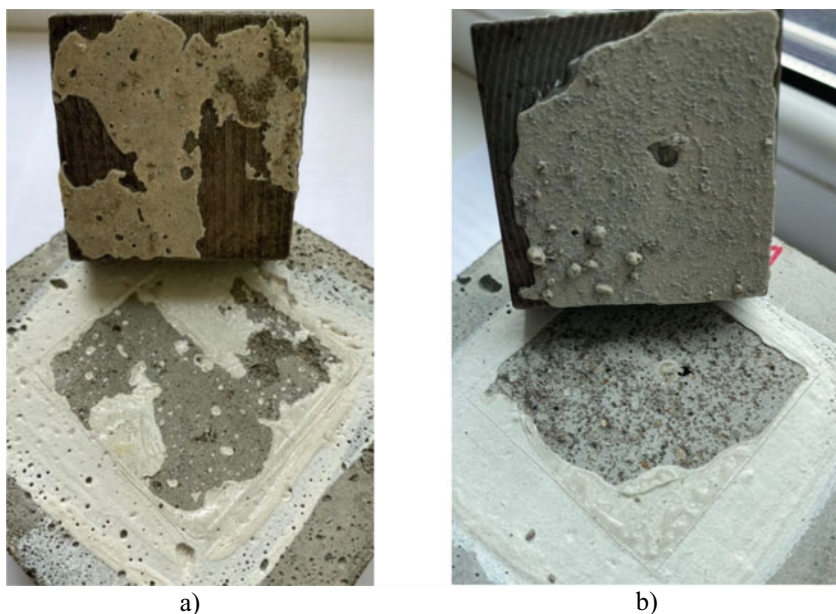


Fig. 6 The result of cleavage of paint coatings filled with the original **a** and activated **b** kaolin from the cement-sand substrate

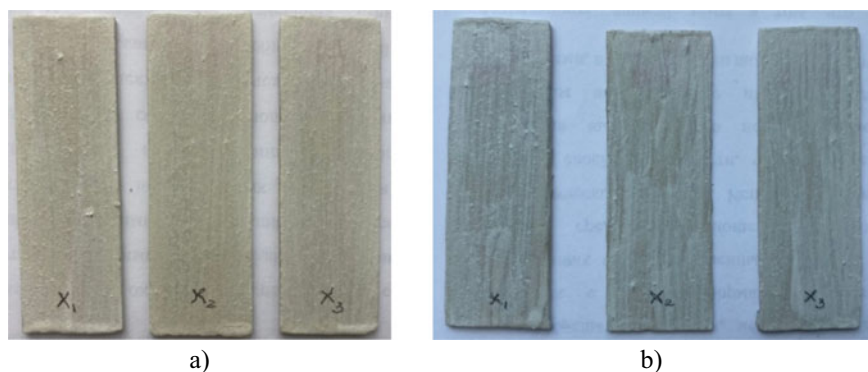


Fig. 7 Surface appearance of paint coatings samples filled by initial **a** and activated **b** kaolin

When exposing PCs samples in aggressive environments (Table 3) it was found that the greatest change in color characteristics occurs in coatings filled with activated kaolin, which is expressed in higher values of the total color difference (ΔE_{ab}^*), compared with the PCs on the original filler. It should also be noted that the coordinates of the coatings shift towards yellow tones (Δb^*), which may indicate chemical aging processes of the styrene component of the film-forming agent [26–28].

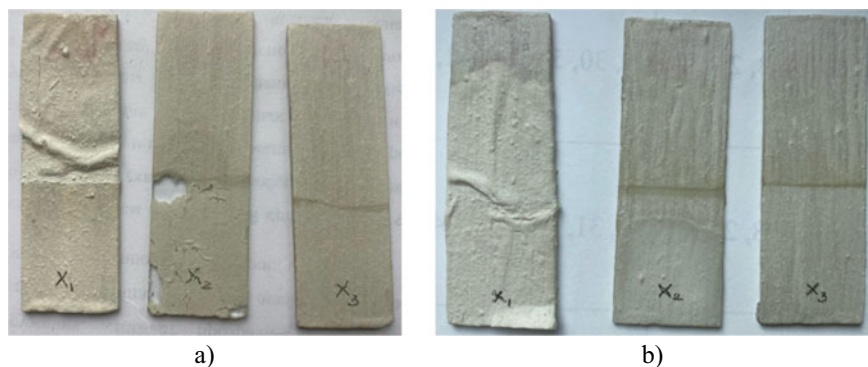


Fig. 8 Appearance of the surface of paint coatings samples filled by initial **a** and activated **b** kaolin after their exposure in aggressive media: x_1 —3% sulfuric acid; x_2 —0.1n sodium hydroxide, x_3 —water

Table 2 The value of the coordinates of the color characteristics of the coating

Exposure media	The value of the coordinates of the color characteristics of the filled coating					
	Initial kaolin			Activated kaolin		
	L	a	b	L	a	b
Initial sample	90	2	2	88	1	0
H ₂ SO ₄	87	3	4	94	1	2
NaOH	87	2	2	86	1	2
H ₂ O	88	2	2	83	2	2

Table 3 The results of calculating the parameters of the color difference of paint coatings after their exposure in aggressive media

Exposure media	Parameter values			
	ΔL^*	Δa^*	Δb^*	ΔE_{ab}^*
Coatings filled by initial kaolin				
H ₂ SO ₄	-3	1	2	3,74
NaOH	-3	0	0	3,00
H ₂ O	-2	0	0	2,00
Coatings filled by activated kaolin				
H ₂ SO ₄	6	0	2	6,32
NaOH	-2	0	2	2,83
H ₂ O	-5	1	2	5,48

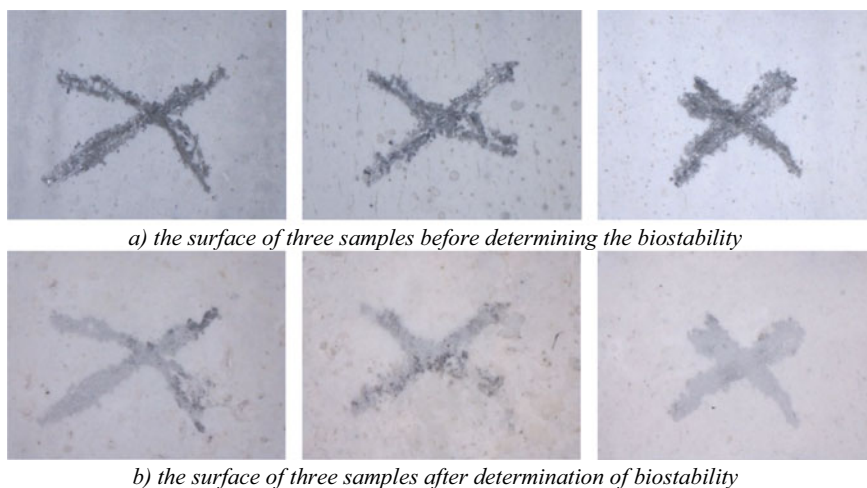


Fig. 9 Photos of the surface of paint coatings samples filled with the initial kaolin before **a** and after **b** determination of their biostability



Fig. 10 Photos of the surface of paintwork samples filled with activated kaolin before **a** and after **b** determination of their biostability

One of the urgent problems of building materials science is biocorrosion. Dozens of buildings and structures are destroyed and lose their functionality every year due to the action of metabolites of microorganisms and mold, which are a mixture of organic acids [29–31]. In this regard, the determination of the resistance of coatings to the action of metabolites of microorganisms—the model medium—was carried out.

It was found that the effect of a model mixture of organic acids contributes to the appearance of microcracks on the surface of the films and their partial destruction, both in PCs samples filled with the initial kaolin (Fig. 9) and activated (Fig. 10).

However, when analyzing the results on the change in the mass of films after their exposure in the model medium, it was found that activated kaolin helps to reduce the sorption of the coating medium by up to 18%, compared with the initial—26%, which, apparently, can be explained by the compacted structure of the formed LPCs.

4 Conclusion

Thus, filling the PCs with kaolin activated in the vortex layer apparatus causes an increase in the level of interaction between the components of the paint composition and their uniform distribution over the coating volume. The formed PCs structure provides an increase in the level of operational indicators: washability—by 3.5 times, water absorption—by 2.5 times and adhesive strength—by 1.5 times. In addition, the introduction of activated kaolin provides an increase in the resistance of coatings to aggressive media and bio-resistance.

The results obtained confirm the effectiveness of the vortex layer apparatus and the prospects of research on the use of the method of activation of fillers in the composition of protective polymer coatings.

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