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Polystyrene paint with reduced contents of volatile compounds

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Abstract. The proposed organomineral additives are novel, eco- friendly components for polystyrene paints. A light brown-red loam was used as a filler for polystyrene paints. Rheological, technological and physico-mechanical properties of paints and coatings based on them were studied by a series of standard tests. Characteristics of frost and water resistance, hiding power and holding capacity of polystyrene paint confirmed the creation of durable paints with high performance properties. Comprehensive studies have shown that the addition of organic additives in the composition of polystyrene paint increases the critical volume concentration of pigment 1.2 times, increases the degree of grinding paint, reduces dispersion time (2 times) and reduces the speed of shelter from 160 to 112 g / m^2. Analysis of the results of experiments showed that the addition of organic additives contributes to increased resistance to external influences, as well as the strength of adhesion to the substrate by 22 %. Using the obtained results will allow you to create polystyrene paints with a low content of volatile compounds and increased crack resistance.

1. Introduction

Every year more and more stringent requirements are imposed on paints and coatings based on them in connection with the advent of new technologies in industry, construction and the formation of modern aesthetic tastes at the consumer. This applies to both the protective and decorative properties of coatings, which are determined by the physicochemical parameters of all components of the paintwork formulation. In recent years, the demand for high-quality products, characterized by increased durability and lower consumption per unit of the painted area, has increased [1–5]. At the beginning of 21-nd century, three factors had a significant influence on the main directions of development of the global paint industry. First, the tightening of environmental legislation on the content of volatile organic compounds (VOC) in paint and varnish products [6–10]. Secondly, it is the search for substitutes for traditional paints and varnishes, which use organic solvents as a basis (mainly solvents and white spirit, as well as drying oil) [11–16]. Thirdly – the economic factor acting in full force in connection with the tightening of environmental legislation. Its action led to a resurgence of interest in the use of powder paints [17–21]. Trends in the development of materials move in the direction of minimizing the solvent content in paint systems, while achieving professional quality that meets all environmental requirements. The advantages of such paints include, first of all, the possibility of their use at low temperatures, which can significantly increase the seasonality of the finishing works. This group of paints is characterized by the formation of a durable and well adhered to a variety of substrates protective film with high rates of frost resistance.

Especially attractive for the use of polystyrene in the paint industry is the comparative cheapness of this polymer, which is associated with the availability of raw materials, simple manufacturing technology, valuable properties [22–26]. Despite the advantages of polystyrene, it is extremely limited in the paint industry. One of the reasons is its high brittleness temperature, which is 90 °C and is almost close to the glass transition temperature of the polymer. In this regard, the difference between the lower and upper boundaries of the temperature range of operation of the coatings is small, which can cause their cracking at low temperatures.

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Nanomaterials (pigments, additives) are effective in all types of coatings (organic, water-dispersed, powder). In the case of polymer nanocomposites, nanoparticulate substances are introduced into the polymer matrix. The role of such substances can be performed by organoclays obtained by modifying montmorillonite clays with an organic additive. The chemical composition of clay causes the presence of inorganic cations on the surface of the plates, giving the surface high hydrophilicity and, accordingly, incompatibility with many polymer resins. For successful formation of a clay-polymer nanocomposite, an appropriate surface treatment should be carried out, reducing the polarity of the clay to make the clay «organophilic» [27–31]. Modified clay (organoclay) has several advantages over simple clay: organoclays are well dispersed in the polymer matrix and interact with the polymer chain. The addition of organoclay into the polymer matrix contributes to the improvement of the mechanical properties of polymers and thermal stability. This is achieved by combining the complex properties of organic (lightness, flexibility, plasticity) and inorganic (strength, heat resistance, chemical resistance) materials.

According [32–39], the process of nanocomposite formation proceeds through a series of intermediate stages (Figure 1).

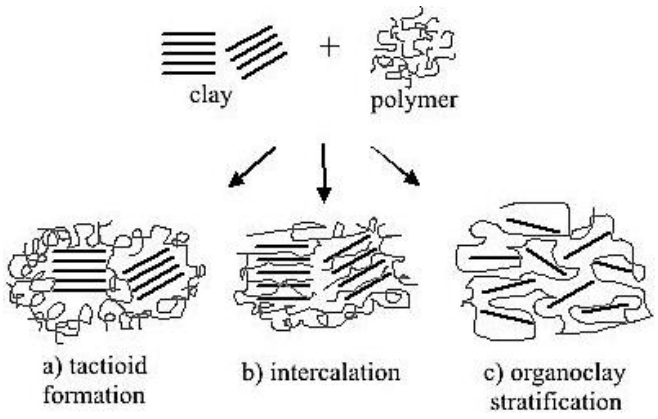

Figure 1. The formation of different morphologies during the dispersion of fillers.

At the first stage, the formation of a tactoid occurs – the polymer surrounds the agglomerates of the organoclay [40–46]. At the second stage (intercalation), the polymer penetrates into the interlayer space of the organic clay, as a result of which the layers expand to 2–3 nm [47–48]. At the third stage (partial exfoliation), partial separation and disorientation of the organic clay layers occurs [49]. At the last stage, peeling occurs [50].

As a scientific hypothesis, a provision has been adopted on the possibility of obtaining an organomineral additive of mixed-layer clay with a high content of montmorillonite. The purpose of this paper is to develop polystyrene paint compositions with a low content of volatile compounds, and coatings based on it, which have enhanced crack resistance.

2. Methods

2.1. Production of organomineral additive

In developing the organomineral additive, clay was used with a specific surface area of 478.3 m^2/kg and an average particle size of 5.01 μm. The specific surface area of clay was determined using the PSH-9 device (Granat, Russia).

The main characteristics and chemical composition of clay are listed in Tables 1 and 2.

Table 1. The main characteristics of clay.

Name of indicator	Value of indicator
Career humidity, %	20–24
Plasticity coefficient	14.3
Total shrinkage, %	5.1
Hygroscopic moisture, %	3.31
Particle size (% by volume): clayey sandy dusty	 11.9–15.8 30–35 49–59

Table 2. The chemical composition of clay.

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	LOI
3.24	65.50	9.54	7.72	0.76	0.06	11.40

As an organic component, several additives were used: sulfanol, Melflux 1641F (BASF, Germany), Melment F15G (BASF, Germany), as well as additives OP-4 and OP-10 (Himbyt, Russia), which are products

of processing a mixture of mono- and dialkylphenols with ethylene oxide and used as wetting and emulsifying surfactants

The plasticizer concentration was determined by changing the surface tension of the plasticizer solution, which was determined by the drip method and was calculated by the formula (1):

$$\sigma = \sigma_s \frac{n_s}{n}, \quad (1)$$

where σ_s is a surface tension of the solvent;

n_s is amount of solvent droplets in 1 ml;

n is number of drops of the solution in 1 ml.

To reduce the time for the manufacture of organomineral additive, it was proposed to prepare the organoclay in a solvent, which was later used to prepare paint formulations.

To determine the amount of surfactant adsorption on the clay surface under the condition σ = const, clay was added to the resulting solution; the solution was mixed and settled for 10 minutes. The time required for the complete adsorption of the OP-4 and OP-10 additives on the clay was determined by the kinetics of changes in the surface tension of the solution. After clay deposition, the surface tension was again checked.

2.2. Design of polystyrene varnishes

For the preparation of polystyrene varnishes were used coal solvent (Severstal, Russia) and oil solvent (Neft, Russia), with equal density of 860 kg/m^3. High impact polystyrene (Salavatnefteorsintez, Russia) was also used. Titanium dioxide, ocher, iron oxide, chromium oxide were used as pigments. Colored sand (Nizhne-Ablyazovskoye deposit, Russia), Omyacarb (Vapenna, Czech Republic), microdolomite (Dolomit, Russia) were used as fillers. Telaz (Avtokoninvest, Russia) was used as a wetting agent. It is an amino acid of vegetable oils, visually a viscous flowing brown liquid, with an amine value of at least 30 mg; is introduced before the dispersion process in the calculation of 5 g per 1 kg of paint.

2.3. Evaluation of the rheological, technological and physicomechanical properties of paint materials and coatings based on them

Conditional viscosity of paint and varnish compositions was determined using a VZ-4 viscometer (Zapadpribor, Russia). The method is based on determining the duration of the expiration (in seconds) of 100 ml of polymer solution through a nozzle with a diameter of 4 mm. The dynamic viscosity of the compositions was also determined using a VZ-4 viscometer. The method is based on the fact that two liquids whose densities ρ_1 and ρ_2, with dynamic viscosity η_1 and η_2, of one volume flow under the action of gravity through the same tube in time t_1 and t_2. This process is described by an equation that follows from the Poiseuille law for laminar fluid flow through capillaries, and has the form:

$$\frac{\eta_2}{\eta_1} = \frac{t_2 \cdot \rho_2}{t_1 \cdot \rho_1}, \quad (2)$$

where η_2 is the dynamic viscosity of the test solution, Pa · s;

η_1 is dynamic viscosity of water, Pa · s;

t_2 is time of leakage of the test solution, s;

t_1 is time of outflow of water, s;

ρ_2 is density of the test solution, g/cm^3;

ρ_1 is water density, g/cm^3.

The value of the dynamic viscosity of the studied finishing composition was calculated on the basis of equation (2), according to the formula (3):

$$\eta_2 = \eta_1 \cdot \frac{t_2 \cdot \rho_2}{t_1 \cdot \rho_1}. \quad (3)$$

The determination of spreadability was carried out according to the follow procedure. Paint with a working viscosity is applied to a metal plate measuring 20 × 40 cm and quickly (no more than 2–3 minutes) distributed by longitudinal and transverse movements of the brush over the entire surface. Then the brush sharply conducts a deep stroke in the middle of the plate from one edge to the other and mark the time when the brush strokes disappear and the surface becomes completely flat. Depending on the time required for the

«filling» of the paint, there are three estimates: 1 – satisfactory (no later than 10 minutes); 2 – slow (10–15 minutes); 3 – unsatisfactory (more than 15 minutes).

The mass fraction of non-volatile substances NV, %, was determined as follows. A paint material was poured into a flat-bottomed metal cup of size 70×110 mm, weighed and evenly distributed along the bottom. Then the paint was dried in a drying oven to constant weight. The mass fraction of non-volatile substances was determined by the formula (4):

$$NV = \frac{(m_2 - m_0)}{(m_1 - m_0)} \cdot 100, \quad (4)$$

where m_2 is a mass of the cup with the dried residue, g;

m_0 is a mass of an empty cup, g;

m_1 is a mass of the test specimen cup, g.

The surface roughness R_a of the coatings was measured using a portable device profilograph TR100 (Time, China), which is based on the principle of feeling the surface of the coating with a diamond needle with a small radius of curvature and the transformation of needle vibrations into voltage changes proportional to these fluctuations.

To assess the adhesion strength, the method of tearing stamp was used (normal tear). The method consists in measuring the force required to detach the coating from the concrete surface with the help of a glued metal stamp of a cylindrical shape with a diameter of 18 mm. The separation force was measured using a dynamometer. Epoxy glue was used to glue the dies to the coating. The adhesion strength of the paint with the substrate R_{adh} was determined by the formula (5):

$$R_{adh} = \frac{P}{F}, \quad (5)$$

where P is a force of detach, N;

F is contact area of the stamp with the paint coating, m².

The tensile strength (cohesive strength) was determined on a tensile testing machine IR 5057-50 (Avtomatika, Russia). The method is based on the tensile test specimen size of 0.7 × 10 × 50 mm to rupture at a deformation rate of 1 mm/min. Specimens of the films were fixed in the clamps of the tensile machine so that its longitudinal axis was located in the direction of tension, and the applied forces acted uniformly over the entire cross section of the specimen. The tests were carried out at air temperature t = 20 ± 2°C and relative air humidity φ = 64 %.

The calculation of tensile strength was carried out according to the results of testing six specimens of each composition. The tensile strength σ_t for each specimen was calculated by the formula (6):

$$\sigma_t = \frac{F_{ti}}{S_{Oi}}, \quad (6)$$

where F_{ti} is tensile load at the moment of rupture, N;

S_{0i} is a initial cross-sectional area of the specimen, m².

The elastic modulus was calculated according to the stress-strain diagram (Figure 2) using the tangent of the angle of inclination to the abscissa axis of the tangent (Z), conducted to the initial straight section of the diagram.

The elastic modulus for each specimen E_i was calculated by the formula (7):

$$E_i = \frac{\sigma_i'}{L_i'} \cdot 100. \quad (7)$$

where σ_i' is the tensile strength at the moment of detach of the tangent from the stress-strain diagram, MPa;

L_i is relative elongation at break, %.

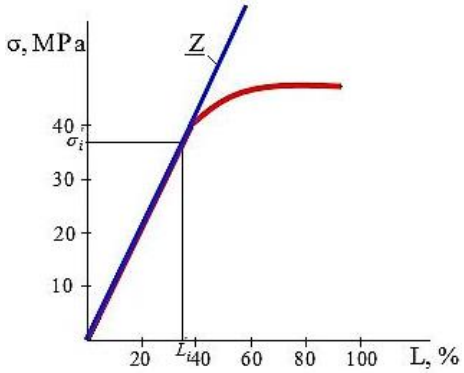

Figure 2. The stress-strain diagram.

The method of measuring internal stresses was as follows. On the disc of aluminum foil with a diameter of 120 mm and a thickness of 0.01 mm applied colorful compositions. A strain gauge with a 50 mm base was glued on the free side of the disk, the readings of which were recorded with an automatic strain gauge based on a digital strain gauge bridge. The value of the stress was determined by the formula (8):

$$\sigma_o = 2\frac{(1-\mu_1)\cdot h_2}{h_1}\cdot E_2\cdot\varepsilon, \tag{8}$$

where μ_1 is Poisson's ratio of paint;

h_1 and h_2 are the thickness of the substrate and the paint coating, m;

E_2 is elastic modulus of the substrate, MPa;

ε is relative deformation of the substrate.

The milling degree was determined by the depth of the Klin device (Grindometer, Russia) groove (in μm) corresponding to the border of a significant amount of individual particles and aggregates of pigments and fillers visible on the surface of the layer of the test material or border the beginning of strokes from them.

The vapor permeability of the coatings was determined using a method based on determining the amount of water vapor that passed through 1 cm^2 of the free-film surface over a period of time at a temperature of 20±2 °C. On the sides of the glass, in which 100 % relative humidity was created, was placed gauze (3 layers) with dried paint, smeared on the edges with paraffin. Periodically the glass was weighed until such time as the weight of the glass with the film did not become constant. The relative humidity of the air in the room was determined using a psychrometer and was 66 %. The coefficient of vapor permeability was calculated by the formula (10):

$$\mu = \frac{P\cdot\delta}{(e_1-e_2)\cdot S\cdot\tau}, \tag{10}$$

here P is the total amount of water vapor passed through the film, corresponding to the increase in film mass during the test, mg;

σ is film thickness, m;

S is film area, m^2;

τ is test duration, h;

e_1 is water vapor elasticity, Pa (at φ = 100 %);

e_2 is water vapor elasticity, Pa (at φ = 66 %).

Resistance to vapor permeability, m^2 · h · Pa/mg, was determined by the formula:

$$R_v = \frac{\delta}{\mu}, \tag{11}$$

here δ is the film thickness, m;

μ is the estimated coefficient of vapor permeability of the material, mg/(m · h · Pa).

The covering power of the paint film was determined as follows. On a pre-weighted glass plate with a size of 200×200 mm put a colorful composition. Then a chessboard was put under the glass plate with the applied paint and with scattered reflected daylight it was observed whether the black and white squares of the chessboard been seen. Covering power (g/m^2) was determined by the amount of paint (in g), followed by coloring the surface of 1 m^2.

The holding capacity of the paint was determined using filter paper. On a filter paper placed on the glass (to avoid additional moisture absorption by the base under the paper), a drop of paint was applied. After 2–3 minutes, the diameter of the drop d_d and the diameter of the wet spot around the drop d_s were measured. The holding capacity of paints was expressed in percent and was determined by the ratio of the diameter of a drop of paint to the diameter of the print of the solvent $d_d/d_s \cdot 100$ %.

The water resistance properties of paint and varnish films were evaluated by the change in the quality of the appearance of the coatings under the action of water. Cement-sand specimens on one side were painted with paint, and on the sides they were treated with paraffin and placed in water. Two hours after removal from the water and air drying, the coatings were inspected and the appearance of white opaque spots, rashes, bubbles, wrinkles, and exfoliation was evaluated. The protective properties of polystyrene coatings were also evaluated by the rate of water penetration through the coating. On painted cement samples were installed flasks with water, treated with clay on the edges. At intervals of time, the amount of water that passed through the coating was measured, and the rate of moisture penetration was plotted against time.

Tests for frost resistance coatings were held in the following mode. Specimens of the cement-sand mortar stained with the proposed composition after saturation in water were placed in a freezer with a temperature of –15 °C and kept for 4 hours, after which they were placed in water with a temperature of 18–20 °C for four hours (one cycle).

2.4. Determination of particle size distribution and sedimentation of clay

The determination of the granulometric composition of clays is based on the ability of clay particles to swell in water and at different rates of falling of particles in water depending on their size (sediometry, or sedimentation rate). Sedimentation analysis is based on observations of the sedimentation rate of particles of the dispersed phase under the action of either gravity or centrifugal force (for systems in which the dispersed phase settles very slowly). The studied powder weighing 1 g was placed in a cylinder with a clean dispersion medium, then stirred evenly by a glass rod with a rubber disk attached at the bottom. Stirring was carried out for 3–5 minutes only in the vertical direction. When mixing, they made sure that no large lumps were left and no air bubbles were formed, as a result of too intensive mixing. After the suspension was thoroughly mixed, the cup was quickly lowered into it to accumulate sediment and hung on the balance arm at height H from the surface of the suspension. Further, sequential measurements were made of the weight of the precipitate during the sedimentation of the suspension using torsion weights device at the following time intervals: 1; 1.5; 2; 2.5; 4; 5; 7.5; 15; 25; 40 (time was taken in minutes).

2.5. Microscope image

The microstructure of clay was examined by polarizing microscope MIN-8 (Scopica, Russia). The microscope is designed to study transparent objects in transmitted ordinary or polarized light with conoscopic and orthoscopic rays.

When using the illuminator on a microscope, studies of opaque objects in reflected polarized and ordinary light were made.

3. Results and Discussion

3.1. Characterization of organomineral additive

It has been established (Figure 3) that with an increase in the concentration of plasticizers, the value of the surface tension decreases to a certain value.

When the concentration of sulfanol and Melment F15G is more than 0.2 %, OP-4 additives – 0.3 %, Melflux 1641F is higher than 0.05 %, stabilization of surface tension values is observed. Thus, the surface tension of a solution with additives at their optimum content is: with sulfanol σ = 29.1, OP-4 σ = 30.1, Melment F15G σ = 64.7, Melflux 1641 F σ = 60.2. Consequently, sulfanol and OP-4 additives have a more plasticizing effect in water.

It is established that the value of adsorption of the OP-4 and OP-10 additives on the clay is 0.38 mg/cm^2 and 0.17 mg/cm^2, respectively (Figure 4).

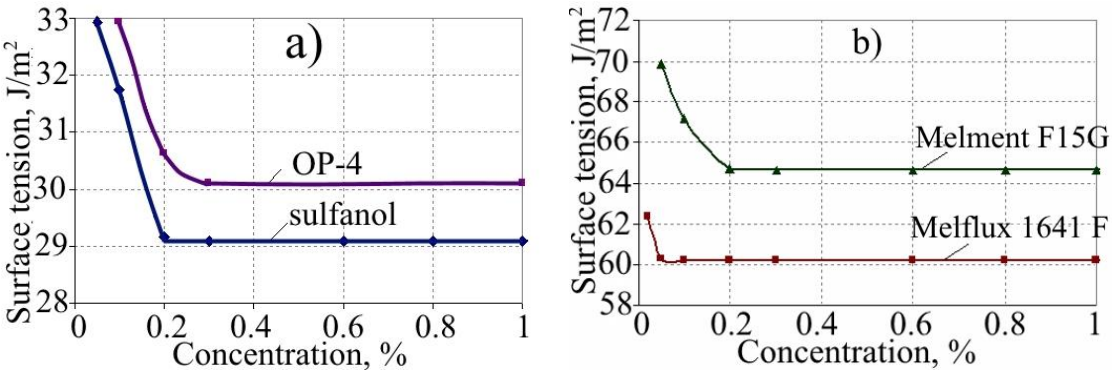

Figure 3. The dependence of the surface tension on the concentration of the additive in water.

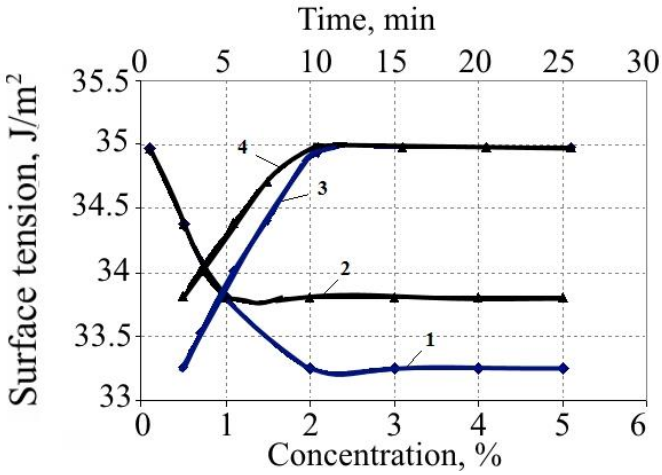

Fig. 4. Dependence of surface tension on concentration additives in the solvent (1, 2) and adsorption time (3, 4): 1, 3 – OP-4; 2, 4 – OP-10.

The subsequent formulation of a solution of polystyrene varnish took into account the amount of the additive adsorbed on the clay.

It has been proposed 2-stage addition of colored filler in the paint composition:

– preliminary mixing of a part of the solvent, OP-4 additives and part of the filler (production of organoclay);

– the subsequent addition of the remaining amount of varnish (solvent and polystyrene) and filler, followed by stirring.

The step-by-step addition of the filler in the mixture with the addition of OP-4 ensures that, at the first stage, in solution of the solvent, the organomineral additive due to the adsorption of the surfactant additives on the surface of clay particles which contained in the colored filler.

The results of the research indicate that the modified clay has a more finely dispersed structure compared to natural clay (Figure 5).

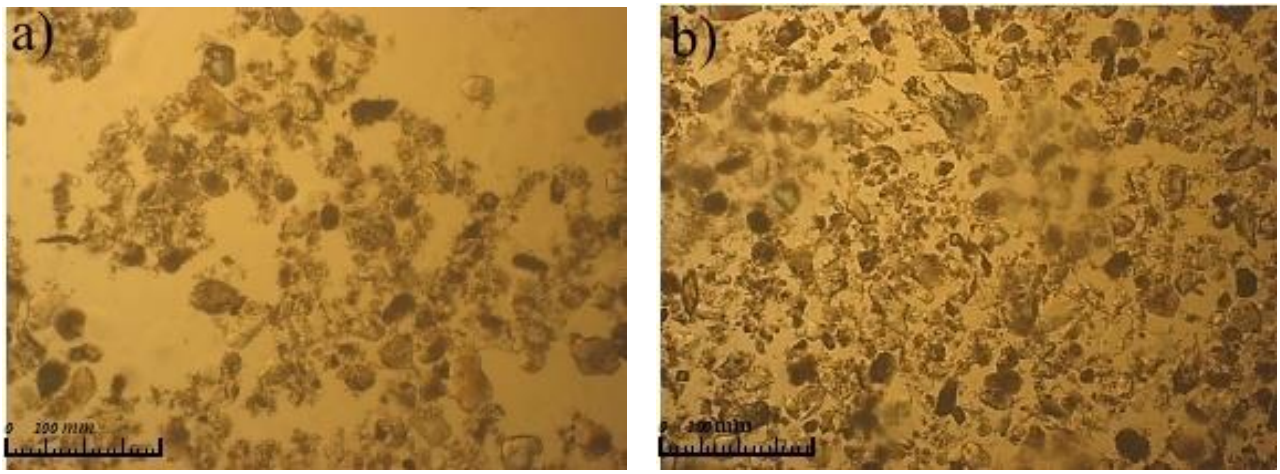

Figure 5. Images of natural (a) and modified (b) clay.

Were developed 2 methods of introducing organoclay in the composition of the paint. In the first method, the technology for preparing a solution with organoclay was as follows. In the solvent, which is used in the preparation of varnish, was introduced additive OP-4. In the resulting solution was added clay in an amount of 2 % by weight of polystyrene. In the second method of lacquer preparation, organoclay obtained in dry form was introduced into the polystyrene melt, which was then used to prepare the lacquer. It has been established that the method of introducing organoclay into the paint leads to a change in the physicotechnical properties of films based on polystyrene varnish. The strength of polystyrene films with organoclay is higher than the controls by 40–45 % with the first method of preparing varnish and 11 % with the second method of introducing organoclay. Due to the high physicotechnical properties, the first method of introducing organoclay into the paint composition was used in the future.

3.2. Determination of the optimal polymer and pigments concentration

In the course of determining the optimal polymer content by changing the viscosity of the polystyrene solution, depending on its concentration in the solvent, it was revealed that the critical concentration of the polystyrene solution in the solvent is 15 %. For further research, the concentration of polystyrene in the solution was 10–15 %.

During the determination of the volume content of pigment in paintwork formulations prepared on the basis of a 10 % solution of polystyrene in solvent, it was found that with the addition of organomineral additives, the values of the critical volume concentration of pigment (COCP) increase compared with the control compositions regardless of the type of pigment (Table 3).

Table 3. The values of the critical volume concentration of pigments.

Composition	COCP			
	TO_2	Ocher	Iron minium	Chromium oxide
control	0.081	0.068	0.083	0.054
with OP-4	0.085	0.071	0.088	0.060
with organoclay, modified OP-4	0.091	0.076	0.093	0.063
with OP-10	0.087	0.072	0.090	0.061
with organoclay, modified OP-10	0.095	0.076	0.096	0.078

At the optimal content of organomineral additives modified by OP-4 and OP-10, an increase in the values of COCP is observed. So, the values of COCP are equal at a control composition of 0.081, for compositions with organoclay – 0.091 and 0.095, which is 12.3 and 17.3 %, respectively.

The optimal degree of filling of polymer composites, calculated on the basis of structural and topological parameters. The results of calculating the consumption of pigments are listed in Table 4.

Table 4. The results of calculations of the consumption of pigments and filler, depending on the topological parameters.

Pigments and filler	Specific surface area, S_{sp}, m^2/kg	Average particle size, d_a, μm	Bulk density ρ_b, kg/m^3	True density ρ_t, kg/m^3	Volume of pigment particles, V, units of volume	Volume of monolithic pigment particles, V_m, units of volume	The volume of the film forming solution, V_f, units of volume
TiO_2, R-2 brand	467.92	3.20	650	4000	0.340	0.054	0.946
TiO_2, CR-02 brand	2053.03	0.73	757	4000	0.040	0.008	0.992
Ocher	1128.83	1.83	730	2900	0.182	0.046	0.954
Iron minium	750.53	2.04	1072	3900	0.209	0.057	0.943
Chromium oxide	1012.64	1.13	882	5210	0.089	0.015	0.985
Colored sand	114.40	21.00	1309	2660	0.883	0.435	0.565

3.3. Effect of organoclay to pigment dispersibility

Modification of clay with the addition of OP-4 leads to a significant increase in its dispersion due to the loosening effect on the structure of layered aluminosilicate, which helps in the process of dispersing in the manufacture of paint to obtain a higher degree of milling at lower energy costs (Figure 6).

It has been established that in paints with organoclay, a milling degree of 23 μm was obtained after 15 minutes of dispersion, and in a control composition (without organoclay), a degree of milling, equal to 25 μm, after 30 minutes. For comparison, Russian organobentonite was introduced into the composition of polystyrene paint. In the composition with organobentonite, a milling degree of 25 μm was obtained after 20 minutes of dispersion.

The addition of the organomineral additive leads to a decrease in the hiding power of the paint from 160 to 112 g/m^2, which is an indirect confirmation of the greater dispersion of the paint.

An additional confirmation of the finely dispersed structure is the experimental data obtained by us on the saturation of the color of the coatings. To describe the color, the HSB color model was used (H is a color tone, S is a saturation, B is a brightness). It is shown that the use of organomineral additive leads to an increase in color saturation from 0.875 to 0.906, i.e. by 3.4 % (while maintaining the values of H and B). Compared with the experimental data of other researchers [2, 8, 10], the shown increase in color saturation is a definite advantage.

3.4. Study of the kinetics of curing coatings

Solvent volatility is one of its most important characteristics. From the speed with which the solvent will evaporate from the surface of the paint film, such characteristics as lightness of feathering the paint, spreading, drying time from «dust» and «full drying», crack resistance, tensile strength depend. The study of the kinetics of solvent evaporation was carried out on paint formulations based on 10 % solutions of polystyrene (Figure 7).

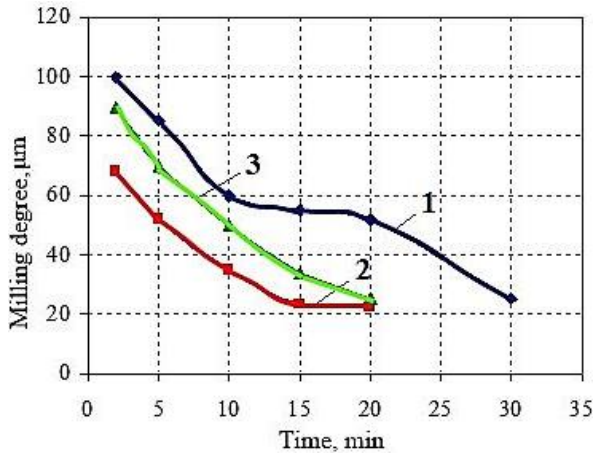

Figure 6. The dependence of the milling degree on the duration of dispersion: 1 – control (without additives); 2 – with organoclay; 3 – with organobentonite.

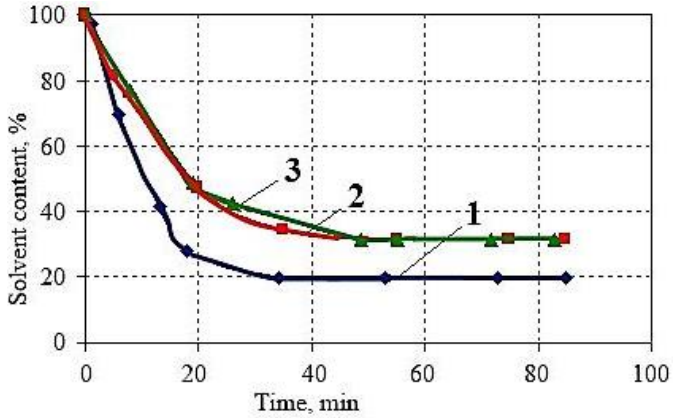

Figure 7. Kinetics of solvent removal from polystyrene paintwork: 1 – control (without additive); 2 – with organoclay; 3 – with organobentonite.

It has been established that at the first stage of coating formation an intensive evaporation of the solvent is observed, leading to a sharp decrease in the weight of the polymer coating. The addition of organomineral additives and organobentonite leads to a slow rate of evaporation of the solvent. In connection with this, the content of volatile compounds decreases in the coloration zone, which makes it possible to increase environmental safety during paint work. In the first 6 minutes of curing the polymer coating, the loss of solvent was 30.56 % for the control composition (without the additive), 18.65 % and 20.12 % for coatings with organobentonite and organic clay, respectively. The content of non-volatile substances of polystyrene paint based on 10 % varnish after 80 minutes of curing is 20 % for the control composition, and 34 % for the composition with organoclay. When using colored sand, the dry residue is 74 %.

It was established that the drying time of coatings to degree 3 on a glass substrate for a control composition is 18 minutes, for compositions with organoclay – 36 minutes; on the cement-sand substrate at the control composition 7 minutes, for compositions with organoclay – 10 minutes. At a negative temperature (T = –10±2 °C) of the cement-sand substrate and a positive paint temperature (T = 20±2 °C), the drying time of coatings based on the control and modified compositions remains almost unchanged. The use of colored filler paint in the formulation leads to a significant increase in the drying time of the coatings.

The slowed down rate of drying of coatings based on modified polystyrene paint leads to a change in its stress state during the curing process. The study of internal stresses in the process of curing the coatings was carried out on paint-and-lacquer compositions with an optimal pigment content (titanium dioxide) at air temperature T = 20±2 °C and relative air humidity φ = 60–65 %. It was established that the growth of internal stresses occurs within 15 minutes, while the evaporation of the solvent was for coatings without additives – 72.22 %, with organoclay – 53.13 %, with organobentonite – 51.43 %. The maximum values of internal stresses are typical for coatings based on control compositions and were σ = 0.05 MPa, with organoclay – 0.016 MPa, with organobentonite – 0.041 MPa. Stress relaxation is observed after 26–30 minutes. The residual values of the internal stresses in the coatings on the basis of the control composition were σ_o = 0.006 MPa, on the basis of the composition with organoclay – 0.005 MPa, on the basis of the composition with organobentonite – 0.013 MPa. Compared to experimental studies of internal stresses obtained by other researchers [36, 43, 48], it decrease of an average of 25–30 % is noted.

3.5. Physical and mechanical properties of varnish films

To study the patterns of change in the deformative properties of coatings based on modified polystyrene paint, free films based on 10 % polystyrene varnish were examined (Table 5).

Table 5. Physical and mechanical properties of varnish films.

Method of organoclay introduction	Composition	Breaking strength σ_b, MPa	Elastic modulus E, MPa	Elastic deformati-ons ε	Plastic deformations ε_p	Relative deformations ε_r
First method	Control	5.24	750	0.56/0.14	3.37/0.86	3.93/1
	Organic clay based on OP-4	9.62	950	0.79/0.28	2.01/0.72	2.80/1
	Organic clay based on OP-10	8.62	810	0.90/0.23	3.10/0.77	4.00/1
Second method	Organic clay based on OP-4	5.91	850	0.65/0.24	2.05/0.76	2.70/1

Note. Above the line, the values of film deformations are given in %, and below the line, the fractions of elastic deformation in the total deformation.

An increase in the elastic deformations of the specimens of films prepared on the basis of compositions using organic clay has been established. Thus, in the control specimens, the elastic deformations amounted to 0.56 %, in the films based on compositions with an organomineral additive modified by OP-4, the elastic deformations increased and amounted to the first method of addition ε = 0.79 % and the second method of addition ε = 0.65 %.

It is shown that with the addition of the organomineral additive polystyrene films have higher values of elastic modulus. In the first method of introducing organoclay, the elastic modulus of the specimens is E = 950 MPa, in the second method of preparing varnish, the elastic modulus E = 850 MPa, while in the control one E = 750 MPa. The addition of organoclay modified with the addition of OP-10 also leads to an increase in the elastic modulus E = 810 MPa.

The reduction of internal stresses in the coatings based on the modified paint and the increase in its cohesive strength contribute to the improvement of their crack resistance. Crack resistance was evaluated by the coefficient of crack resistance, which was determined as the ratio of the internal stresses of the coatings to the tensile strength of the films. It was revealed that the use of organic additives in the formulation of polystyrene paint leads to an increase in crack resistance by 2 times compared with the control composition (without additives).

Addition to the formulation of polystyrene paint organomineral additives reduces the time of flowing property from 10 to 3–4 minutes, increasing the holding capacity by 13 %, which contributes to a better applicability of paint on cement surfaces and improve the quality of the appearance of coatings, which were evaluated, as well as in terms of surface roughness. It is revealed that the surface roughness of the coating based on the control composition is R*a* = 0.74–1.2 μm, and the surface roughness of the coatings based on the composition with organic clay are R*a* = 0.4–0.6 μm.

The addition of organic additives leads to an increase in adhesion strength by 22 %. The adhesive strength of the control specimen was 1.88 MPa, and with organoclay – 2.42 MPa. Replacing 5 % of the titanium dioxide pigment with Omyacarb fillers and microdolomite leads to a decrease in the adhesion strength of the coatings to the substrate by 4.5 and 12 % compared with the composition without filler. It was studied the effect of the addition of organomineral additives on the water resistance of coatings, which was determined by the kinetics of moisture penetration through the coating, as well as by the change in the quality of the appearance of the coatings after 24 hours in water. It was established that the presence of organoclay in the formulation of paint helps to reduce the rate of penetration of moisture. The maximum speed of moisture penetration through the coating is after 72 hours for formulations with organogline of 0.0057 mg/h, and for the control composition (without organoclay) – 0.0125 mg/h. The maximum moisture penetration rate is characteristic of coatings based on paint with a filler, which characterizes a more porous structure of the coating. This is confirmed by the results of studying the porosity of paint coatings. It was revealed that the replacement of 5 % titanium dioxide by microdolomite leads to an increase in large pores of the coating. The relative total porosity with an equivalent radius of 50 to 99 μm was 54.8 % for the composition without filler and 56.0 % for the composition in which part of the pigment was replaced with microdolomite.

It is shown that the coatings based on the control composition (without organoclay) have a color change, appearance of stains, rash on 20 % of the surface after 288 hours in water, while the coating on the basis of the composition with an organomineral additive changes color without showing surface defects occurred only

after 512 hours of testing. The addition of fillers in the formulation of the paint composition contributed to a certain decrease in the waterproof properties of the coatings. Discoloration, the appearance of spots and rashes on the surface of the coatings appeared only after 360 hours of testing (for formulations with microdolomite) and 312 hours (for formulations with Omyacarb).

The presence of organic additives in the formulation of polystyrene paint leads to a change in the hydrophysical properties of coatings.

The resistance to vapor permeability of the control composition (without an organomineral supplement) was $R_v = 6.40 \cdot 10^5$, and with organic clay $R_v = 8.50 \cdot 10^5$. The resistance to vapor permeation of polymer coatings based on paints filled with microdolomite and Omyacarb are almost 1.5 times lower than the resistance to vapor permeation of polymer films based on paints without filler.

Addition to the formulation of paint organic supplement leads to an increase in the frost resistance of coatings. Coatings based on the control composition collapsed after 112 cycles of alternate freezing and thawing. Coatings based on the composition with organoclay after 160 cycles collapsed.

Based on comprehensive studies, an optimal formulation of polystyrene paint with an organomineral additive based on clays from local quarries has been developed. Table 6 shows the formulation of polystyrene paints with a rational content of pigment and filler.

Table 6. Formulations of polystyrene paints.

Components	Composition of polystyrene paints (wt. %)				
	control	with organomineral additive			
		I	II	III	IV
Polystyrene	7.9	7.8	7.8	7.8	4.5
Solvent	70.7	70.4	70.4	70.4	25.8
Pigment	20.9	21.3	20.23	20.23	–
Color sand	–	–	–	–	68.94
Microdolomite	–	–	1.07	–	–
Omyacarb	–	–	–	1.07	–
Clay	–	0.2	0.2	0.2	0.09
Additive OP-4	–	0.3	0.3	0.3	0.17
Telaz	0.5	–	–	–	0.5

Table 7 shows the comparative characteristics of polystyrene paints of the control composition (without additives) and composition with organoclay.

Table 7. Exploitational properties of polystyrene paints and coatings based on them.

Indicator	Control	I	II	III	IV
Relative viscosity, s	15–20	25–30	25–30	25–30	140–160
Drying time at (20±2) ºC, min, not more than	7–9	10–12	9–12	8–10	12–14
Milling degree, μm, not more	50	22	25	25	-
Resistance to static exposure to water at (20±2) ºC, h, not less	48	72	48	48	24
Resistance to vapor permeability $R_v \cdot 10^{-5}$, $m^2 \cdot h \cdot Pa/mg$	6.4	8.5	5.8	6.0	4.2
Adhesion strength, MPa	1.88	2.42	2.11	2.31	1.36
The nature of the surface finishing layer	smooth				textured
The quality of the external coating after 500 hours of moisturizing	loss of luster up to 50 %, dis-coloration, haziness, significant dirt retention, cracks or surface meshes, visible to the naked eye, flaking, no bubbles	loss of luster up to 5 %, color change is barely noticeable, haze is absent, grinding is barely noticeable, weathering, cracking, bubbles and exfoliation are absent	loss of gloss up to 20 %, dis-coloration, bronzing, haze, dirt retention are in-significant	IV.7	loss of luster up to 50 %, dis-coloration, haziness, significant dirt retention, cracks or surface meshes, visible to the naked eye, flaking, no bubbles (after 200 h)
Covering power, g/m^2	160	112	142	110	–
Frost resistance, cycles	112	160	138	132	18

Thus, the use of colored filler in the formulation of polystyrene paints gives the surface of coatings textured character, expands the decorative range of finishes.

4. Conclusion

A novel organomineral additive for the polystyrol paint with reduced contents of were prepared and characterized to determine its volatile compounds characteristics. Based on the results of various tests, the following conclusions were drawn:

1. The composition and technology of producing an organomineral additive designed for polystyrene paints as a structuring and dispersing additive, which is a mixed-layer clay with an adsorbed surfactant – the product of the interaction of alkylphenols with OP-4 ethylene oxide, has been developed. It is established that the value of the adsorption of the OP-4 additive on the clay is 0.00038. Methods for the addition of organomineral additives in the formulation of polystyrene paint are proposed.

2. The use of colored sand as a filler in polystyrene paints, which is a mixture of quartz sand and clay (up to 11 %) and has a red-brown color, is substantiated. It is proved that, on the basis of the specified filler, it is possible to obtain a solution of an organomineral additive by adsorbing an OP-4 additive on the surface of the clay particles contained in the colored filler. Based on the results of complex studies, it has been found that the addition of the organomineral additive into a polystyrene paint formulation increases the critical pigment volume concentration by a factor of 1.2, increases the degree of paint milling, reduces dispersion time (by 2 times), and decreases the hiding rate from 160 to 112 g/m^2.

3. The composition of polystyrene paint with a low content of volatile compounds, designed for exterior and interior decoration of building products and structures. It was revealed that the modified polystyrene paints have the best filling, increased by 13 % retention capacity (relative to the solvent). Coatings based on the developed polystyrene paint have improved crack resistance and appearance qualities. The main protective properties of coatings based on modified polystyrene paint are determined. It is shown that the addition of organic additives contributes to increased resistance to external influences, as well as the strength of adhesion to the substrate by 22 %.

4. The regularities of the influence of the organomineral additive on the technological properties of polystyrene paint and varnish compositions, which consist in increasing the drying time of coatings on the cement-sand substrate by 30 %, are established. Drying time at a low temperature for compounds with organoclay increases by 12.5 %. The regularities of the influence of the organomineral additive on the strength, deformative properties of coatings are established, namely, the addition of the organomineral additive in the polystyrene paint formulation leads to an increase in cohesive strength of 1.6–1.8 times, the elastic modulus 1.2 times, the proportion of elastic deformation 2 times and reduce the proportion of plastic deformation in the total deformation of the coatings. The regularities of changes in internal stresses in coatings based on polystyrene paint are established. It has been shown that the addition of the paint of an organomineral additive into the formulation leads to a decrease in internal stresses by a factor of 2.

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Полистирольная краска с пониженным содержанием летучих соединений

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Ключевые слова: здания; строительство; органоминеральная добавка, полистирольная краска, глина, летучие органические соединения

Аннотация. Предложенные органоминеральные добавки являются новыми, экологически чистыми компонентами для полистирольных красок. В качестве наполнителя для полистирольных красок использовался легкий суглинок коричнево-красного цвета. Реологические, технологические и физико-механические свойства лакокрасочных материалов и покрытий на их основе изучались серией стандартных испытаний. Характеристики морозо- и водостойкости, укрывистости и удерживающей способности полистирольной краски подтвердили создание долговечных красок с высокими эксплуатационными свойствами. Комплексные исследования показали, что введение органоминеральной добавки в состав полистирольной краски увеличивает критическую объемную концентрацию пигмента в 1,2 раза, увеличивает степень измельчения краски, уменьшает время диспергирования (в 2 раза) и уменьшает скорость укрытия со 160 до 112 г/м^2. Анализ результатов экспериментов доказал что введение органических добавок способствует повышению устойчивости к внешним воздействиям, а также прочности сцепления с подложкой на 22 %. Использование полученных результатов позволит создавать полистирольные краски с пониженным содержанием летучих соединений и повышенной трещиностойкостью.

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