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MODELING THE WETTING OF TITANIUM DIOXIDE AND STEEL SUBSTRATE IN WATER-BORNE PAINT AND VARNISH MATERIALS IN THE PRESENCE OF SURFACTANTS

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This paper reports the results of studying the effect of two additives such as polyether siloxane (PS) and sodium polyacrylate (SPA) on the wetting of various substrates in water-borne paints (WB paints).

Titanium dioxide (TiO_2), paraffin (PA), steel (ST), and glass (GL) were used as solid substrates. The edge wetting angle (θ0) and the ratio (dCosθ/dCS) were used as the criterion for assessing the wettability of solid substrates. In aqueous solutions (without acrylic resin), both surfactants improve the wetting of the substrates. For PS, all the substrates studied, depending on θ depression, can be arranged in a row: ST>PA>GL>TiO_2.

For SPA: PA>TiO_2>GL>ST. The introduction of an acrylic film-forming agent in the composition enhances the wetting ability of SPA (in comparison with the aqueous solution of surfactants). With an increase in the concentration of SPA from 0 to 4 g/dm^3 in acrylic resin solutions, the edge wetting angle of steel decreases by 6÷8° (while in water by only 3°).

With respect to TiO2, the wetting activity of SPA does not depend on the acrylic content of the water. PS in acrylic-containing compositions exhibits worse wetting activity than SPA. The introduction of surfactants in the compositions improves the quality of coatings. With optimal SPA contents in the compositions, the corrosion rate of coatings is reduced (in distilled water by 45 %, in 60 % NaCl solution by 60 %). At the same time, the gloss of coatings increases by 50 % while adhesion increases by 2 points (according to ISO 11845:2020). This is fully correlated with the nature of the effect of surfactants on the wetting of the steel substrate and pigment (titanium dioxide). Based on probabilistic-deterministic planning, the compositions of WB paints were optimized, ensuring their maximum wetting of TiO_2 and ST. Equations for calculating cosθ depending on the content of acrylic polymer and surfactants have been derived

Keywords: wetting of coatings, surfactants, water-borne paints, organic coatings

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1. Introduction

When using paints and varnishes, great attention is paid to environmental aspects [1], which leads to a large-scale replacement of organ-dilute paints with water-borne ones. In technological practice, there are primary and secondary aqueous dispersions of polymers [2], in which the dispersed phase consists of spherical polymer particles with a diameter of less than 1 μm, and the dispersion medium is water. In the paint and varnish industry, the most common is primary dispersions obtained by emulsion polymerization (WB paints). For example, in work [3], as a result of emulsion polymerization, in contrast to polymerization in solution (secondary dispersion), polymer macromolecules contained inside the particles of the dispersed phase were obtained. This makes it possible to use high-molecular polymers as film formers for WB paints, which cannot be used in the form of solutions due to their high viscosity. As evidenced by world experience [4], the formulations of WB paints are dominated by aqueous dispersions of acrylic copolymers, acryl styrene copolymers, homo- and copolymers of vinyl acetate. Due to the multi-stage synthesis processes, polyacrylates are more expensive than styrene and vinyl acetate but have several significant advantages. Acrylic coatings are almost transparent to ultraviolet rays, so the processes of destruction of the film former in them occur much more slowly, as a result of which they are not prone to yellowing and retain shine with prolonged atmospheric exposure. However, despite the advantages of acrylic coatings, they, like all water-borne paints, are inferior to organ-dilutable ones in terms of anti-corrosion properties [5].

Work [6] shows that the organization of reliable and long-term corrosion protection of coatings is one of the priority tasks in the VD-paint technology. Modern technological solutions are focused on the introduction into their composition of surfactants that have the ability to change the surface energy of film formers at the interfaces with the contacting phases (air, steel substrate, pigment). Minimization of surface energy contributes to better wetting of pigment particles when they are combined with the film-forming one, which makes it possible to obtain dense, impermeable to aggressive environments insulating films. In addition, an increase in the wetting capacity of the paint compositions of the steel surface increases the adhesion of the coatings formed by them. High adhesive strength, in turn, prevents the formation and spatial growth of corrosion products under the WB paints film, which improves the protective ability of coatings.

The relevance of our scientific area is due to the need to study the effect of surfactants on the wettability of pigments and steel substrates with solutions of acrylic resins in the composition of WB paints. The results of these studies are important for the industry as they would create new environmentally friendly anti-corrosion WB paints, with an increased protective resource of operation. These acrylic paints could well be used in everyday life and industry for painting various surfaces.

2. Literature review and problem statement

There are no universal wetting modifiers for WB paints. The wetting properties of surfactants are related to their chemical composition and conformational structure and depend on the qualitative and quantitative characteristics of the dispersion medium and solid-phase components. For the effective use of modifiers in certain paint compositions, it is necessary to conduct thorough research in the field of physical and chemical mechanics and colloidal chemistry. It follows from [7, 8] that, as a rule, the selection of modifiers is carried out for each individual case and without taking into consideration the regularities of the influence of the nature of the binder, pigment, and surfactant on the effectiveness of modification.

In addition, a purely empirical approach to the dosage of the modifier is characteristic. There is no generally accepted theory of the selection of surfactants for various paints depending on the parameters of the solubility of the polymer and solvent, their polarity, surface properties of pigments and fillers.

Work [8] shows that the use of additives in paint compositions can be of a dual nature.

First, some additives are effective in certain paint systems, and in others, they are already ineffective (or even harmful). Second, the introduction of additives often leads to undesirable effects if they are used in concentrations higher than optimal. For example, surfactants are introduced into paints to improve wetting of the pigment surface but lead to foaming processes, which are corrected by another additive (silicone solution). Paper [9] shows that the duration of the protective resource of paint and varnish products is determined by the supramolecular structure and the size of the solid-phase particles of the pigment, while all these parameters are regulated by the content of surfactant additives in the paints. The influence of the type and concentration of the additive on the change in interfacial energy and the stability of dispersed systems is demonstrated. It is proved that surfactants in paint compositions improve the aggregate and sedimentation stability of suspensions. However, the reasons for the improvement of these indicators are not substantiated. Study [10] shows that in various paint compositions, the introduction of surfactants makes it possible to obtain coatings with the most uniform distribution of pigment particles in the polymer matrix, due to the maximum stability of the "film-pigment-surfactant" suspensions. Moreover, for these coatings, the maximum is observed of protective resource, optical properties, gloss, concealment, and other characteristics. Paper [11] shows that the introduction of surfactants into paints causes an increase in the number of adhesive contacts, as a result, the protective resource of paint coatings increases.

The introduction of surfactants into paints is characterized by a decrease in surface energy at the interphase boundary of "film-forming agent/pigment" and "film-forming agent/substrate" [12], which leads to an increase in wetting of pigment particles and substrate with a solution of film-forming particles. However, the cited study does not propose criteria for assessing the wettability of pigments. Study [13] shows that in order to quantify the change in the wetting of the pigment with a film-forming solution, it is advisable to use the calculated value – the work of adhesion. The positive side of the cited work is the improvement of the indicators of wetting titanium dioxide with film-forming solutions (reducing the edge angle of wetting) as the adhesion increases. At the same time, the cited paper did not study the effect of surfactants on the work of adhesion.

The difficulty of choosing surfactants for paint systems is primarily due to the fact that such systems are extremely difficult to generalize. The use of methods of probabilistic-deterministic modeling (PDM) makes it possible to tackle this issue.

3. The aim and objectives of the study

The purpose of this study is to optimize the wetting of titanium dioxide and steel substrate with solutions of acrylic resins, by regulating the content of surfactants and film-forming agents in the paint, with the construction of a mathematical model of the process. This will make it possible to obtain environmentally friendly water-borne paints, with the maximum possible protective characteristics of coatings.

To accomplish the aim, the following tasks have been set:

– to determine the effect of surfactant content on wetting various substrates (steel, titanium dioxide, paraffin, and glass) with water;

– to study the effect of surfactant and acrylic film-forming agent content on the wetting of water-borne compositions of various substrates (steel, titanium dioxide, paraffin, and glass);

– to study the effect of the content of surfactants and an acrylic film-forming agent on the work of adhesion (W_a) of solutions of water-borne compositions on steel;

– to conduct mathematical modeling of the effect of the concentration of surfactants and an acrylic film-forming agent on the wetting process;

– to assess the effect of surfactants on the anti-corrosion characteristics of modified formulations.

4. The study materials and methods

When conducting research, the following were used:

1. As a film-forming agent – acrylic compositions based on water-borne dispersion (TU 2316-014-88753220-2006).
2. As surfactants: polyether siloxane (PS) and sodium polyacrylate (SPA).
3. As substrates for determining the edge angle of wetting of the plate (26 mm×76 mm) of the following materials:

– steel according to GOST 16523-97;

– pigment dioxide of titanium grade R-02 ((GOST 9804-84) of rutile form (mass fraction of titanium dioxide of rutile form – 95 %), manufactured at ChAO "Crimean TITAN", Ukraine);

– paraffin according to GOST 23683-89;

– glass according to TU 21-0284461-058-90.

Binary and triple systems were investigated: "water-surfactant", "water-film-forming agent-surfactant". Aqueous solutions with a given concentration of surfactants (C_S=0.25÷4 g/dm^3) were prepared by sequential dilution of the initial solution (C_S=4 g/dm^3) with distilled water. Surfactant solutions with a concentration of 4 g/dm^3 were obtained by dissolving the batch of additives in distilled water. In water-borne compositions (C_{FFA}=10÷30 %) the same quantitative contents of surfactants as water varied (C_S=0.25÷4 g/dm^3).

The edge angle of wetting was determined on four types of solid surface. Glass was used as a reference for the polar surface, paraffin – non-polar. When choosing a steel plate, we proceeded from the positions of maximum approximation to the real conditions for applying paints.

The procedure for measuring the edge angle of wetting was as follows.

The ability of surfactants to influence the interaction of the liquid with a solid surface (in the presence of simultaneous contact with air) was assessed on the basis of determining the edge angle of wetting (θ) at a fixed temperature (T=293 K). θ measurement was carried out using the ACAM series automatic dynamic wetting angle measurement system (Fig. 1).

Hamilton's 0.25 ml syringe (Gastight, 1725 RN, Hamilton) was filled with the test solution and placed in dispenser module 1. After turning on the main controller 8 and the engine of the dispenser module 10, the ApexAcamSoftware program was launched (Fig. 2). Then, with the light intensity control 3 (Fig. 1), an absolutely white background was achieved, as shown in Fig. 2, for the purpose of accurate calculation of the contact angle.

Using the needle adjustment system 9 (Fig. 1), horizontally and vertically, the centering of the tip of needle 2 (Fig. 2) was achieved. A shadow image of the droplet was obtained using a high-speed C-mount camera, CCD-type 6 (Fig. 1).

The study of the spread of the drop was carried out during the implementation of forced injection and pumping of liquid to the substrate by a system consisting of the main controller 8, engine 10, and the dispenser module 1 (Fig. 1). The feed rate of 5 µl/s and the droplet volume of 10 µml were set constant by setting the appropriate values in the Setparameters tab of the software (Fig. 3).

A drop of the required volume, from the tip of the needle of Hamilton's syringe, was transferred to the substrate, raising the table up until the drop came into contact with the surface (Fig. 4).

Fig. 1. Automatic system for measuring the dynamic wetting angle of ACAM series: 1 — module of the dispenser ADCAM-02; 2 — light source; 3 — light intensity control; 4 — base; 5 — table raising regulator; 6 — camera; 7 — table with a substrate; 8 — chief controller; 9 — horizontal and vertical needle adjustment systems; 10 — engine of the dispenser module

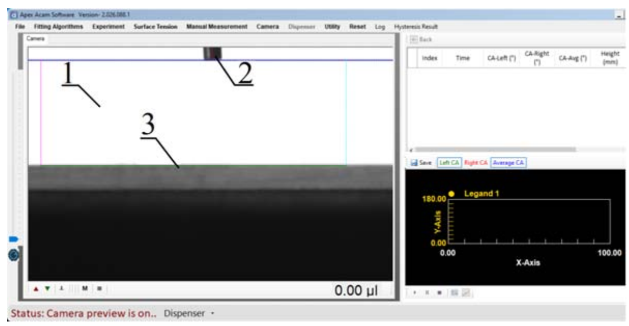


Fig. 2. Adjusting the intensity of the white background and the centering of the needle using ApexAcamSoftware: 1 — white background; 2 — needle alignment; 3 — substrate

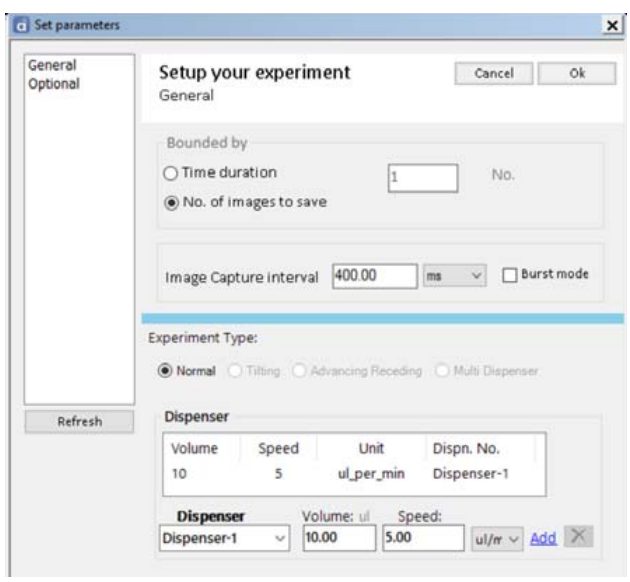
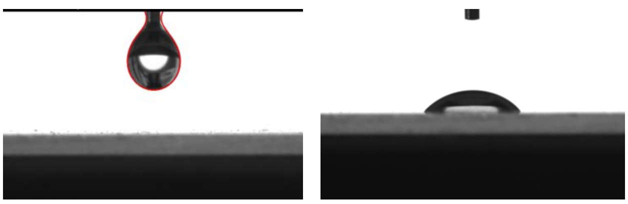


Fig. 3. Set parameters tab of Apex Acam Software



a *b*

Fig. 4. The process of acquiring an image of the droplet: *a* – the process of transferring a drop of solution from the tip of the needle; *b* – to the surface of the substrate

Static contact angles in the equilibrium state were measured 20 seconds after dosing, according to the recommendations from [14]. The shadow two-dimensional image of the droplet was processed by a circular method (Fig. 5).

The essence of the method is to capture and save the image from the fallen droplet. The algorithm for determining the edge angle of wetting includes the following three operations:

1. Baseline recognition 1 (Fig. 5).
2. Selection of points at the edge of the curvilinear profile of droplet 2 (Fig. 5).
3. Finding the equation of the circle and the angle of the tangent to the baseline at the two points of intersection of the circle with the baseline, which is the angle of wetting.

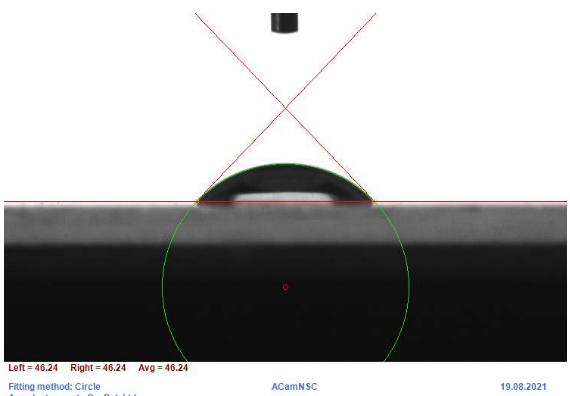


Fig. 5. Finding the edge angle of wetting using ApexAcamSoftware

The edge angle of wetting was determined by five parallel measurements, the average values are reported. The measurement accuracy was ±0.05°.

Modeling of the joint effect of surfactants and a film-forming agent on the wetting ability of water-borne compositions was carried out in line with the method of probabilistic-deterministic planning (PDP) [15]. A detailed description of the process of applying the PDP method for modeling multifactorial processes is shown in work [16].

Research work using PDP consisted of several stages:

1. As input factors, the following were determined: the content of acrylic dispersion in the aqueous solution (C_{FFA}, %: 0÷30), and the concentration of surfactants (C_S, g/dm^3:0÷4). The numerical values of the levels for each factor are given in Table 1.

Table 1

Numeric level values for each factor

Factor	Level					
	1	2	3	4	5	6
C_S, g/dm^3	0	0.25	0.5	1	2	4
C_{FFA}, %	0	10	20	30	–	–

2. They compiled an orthogonal plan-matrix of a two-factor experiment 4×6. Taking into consideration the different number of levels of the two input factors, the total number of experiments would be 4*6=24. The accepted response function was the cosine of the edge angle of wetting (here, *i* is the serial number of the experiment).

Table 2

Orthogonal plan-matrix of a two-factor experiment

Level of factor C_S, g/dm^3	Level of factor C_{FFA}, %			
	0	10	20	30
0	y_1	y_7	y_{13}	y_{19}
0.25	y_2	y_8	y_{14}	y_{20}
0.5	y_3	y_9	y_{15}	y_{21}
1	y_4	y_{10}	y_{16}	y_{22}
2	y_5	y_{11}	y_{17}	y_{23}
4	y_6	y_{12}	y_{18}	y_{24}

3. We conducted a series of experiments according to the plan-matrix (Table 2) and formed an experimental array, setting the numerical values of the response functions (output parameters) for each experiment.

4. We sampled an experimental array for each level of each factor according to Table 3.

Table 3

Sample of the experimental array

Level of factor C_S, g/dm^3	Sample	Level of factor C_{FFA}, %	Sample
0	$(y_1+y_7+y_{13}+y_{19})/4$	0	$(y_1+y_2+y_3+y_4+y_5+y_6)/6$
0,25	$(y_2+y_8+y_{14}+y_{20})/4$	10	$(y_7+y_8+y_9+y_{10}+y_{11}+y_{12})/6$
0,50	$(y_3+y_9+y_{15}+y_{21})/4$	20	$(y_{13}+y_{14}+y_{15}+y_{16}+y_{17}+y_{18})/6$
1,00	$(y_4+y_{10}+y_{16}+y_{22})/4$	30	$(y_{19}+y_{20}+y_{21}+y_{22}+y_{23}+y_{24})/6$
2,00	$(y_5+y_{11}+y_{17}+y_{23})/4$	–	–
4,00	$(y_6+y_{12}+y_{18}+y_{24})/4$	–	–

Based on a sample of an experimental data array (Table 3), partial dependences of response functions on the content of the film-forming agent and the concentration of the surfactant were constructed.

6. Each partial dependence was approximated by a function of one variable, then these functions were combined into a multifactorial statistical mathematical model (generalized equation) based on the semi-empirical formula (1) proposed in [17]:

$$Y_0 = \frac{\prod_{i=1}^{p} Y_i}{Y_{av}^{p-1}}, \qquad (1)$$

where Y_o is a generalized equation; Y_i is a private function; $\prod_{i=1}^{p} Y_i$ – the product of all particular functions; *p* is the number of particular functions equal to the number of input factors; Y_{av}^{p-1} is the arithmetic mean of all the considered experimental values of the response function (general mean) to the power of one lesser number of particular functions.

7. The accuracy of the obtained multifactorial statistical mathematical models was evaluated by calculating the coefficients of nonlinear multiple correlation (R) from (2):

$$R=\sqrt{1-\frac{(n-1)\cdot\sum_{i=1}^{n}(y_i-\hat{y}_i)^2}{(n-p-1)\cdot\sum_{i=1}^{n}(y_i-\bar{y})^2}},\qquad(2)$$

where n is the number of experiments; p is the number of input (independent) parameters; i is the serial number of the experiment; y_i is the actual value of the output parameter in the i-th experiment; $\hat{y}_i$ – the estimated value of the output parameter, calculated using a multifactorial mathematical model, for the conditions (values of the input parameters) of the i-th experiment; $\bar{y}$ – the average value of the actual value of the output parameter for all n experiments (general average).

The significance of the calculated coefficient of nonlinear multiple correlation was confirmed using the Student's criterion.

The effect of surfactants on the adhesion of water-borne paint to the surface of the steel substrate was evaluated by the "work of adhesion W_a (J/m^2)". The work of adhesion was calculated on a steel substrate, due to the need to trace the effect of surfactants on the anti-corrosion properties of coatings. The work of adhesion was found according to the combined Dupré-Young equation:

$$W_a=\delta_{l-g}\times(1+\cos\theta),\qquad(3)$$

where δ_{l-g} is the surface tension at the boundary "solution of water-borne composition/air", J/m^2; θ is the edge wetting angle of the steel substrate (degrees).

The corrosion rate was determined in distilled water and 60 % NaCl solution (by weight) in accordance with ISO 11845:2020 (en) on steel plates of 65×25×1 mm (length×width×thickness). The test time was 60 minutes.

Corrosion rate as a function of time was calculated using the equation:

$$V_k=\frac{m_1-m_2}{S\times t};\qquad(4)$$

where m_1 is the weight of the immersion plates in the solution of the test medium, g;

m_2 is the weight of plates after immersion in the solution of the test medium, g; S=0.00325 is the full plate area, m^2; t is the test time, in hours.

The corrosion rate was determined by the gravimetric method (weighing the plates before and after holding in the test solution).

The adhesion of the coatings to the steel substrate was assessed in accordance with ISO 11845:2020 on steel plates measuring 150×70×2 mm (length×width×thickness) in natural (sunlight) light. The coating was applied to the plates by pouring and kept for 24 hours at a temperature of 20±5 °C. All samples were examined at least 5 times. The results show averages.

The gloss of coatings was determined in accordance with ISO 2813:1994 on the gloss gauge BF5–60/60, according to the instructions for the device.

The appearance of the coatings was evaluated on steel plates measuring 150×70×2 mm (length×width×thickness) in natural (sunlight) light. The coating was applied to the plates by pouring and kept for 24 hours at a temperature of 20±5 °C. All samples were examined at least 5 times.

5. Results of the pigment wettability study

5. 1. Studying the edge angle of wetting with water of various substrates in the presence of surfactants

The effect of surfactant concentrations in water on the edge wetting angles (θ) is expressed by the dependences shown in Fig. 6.

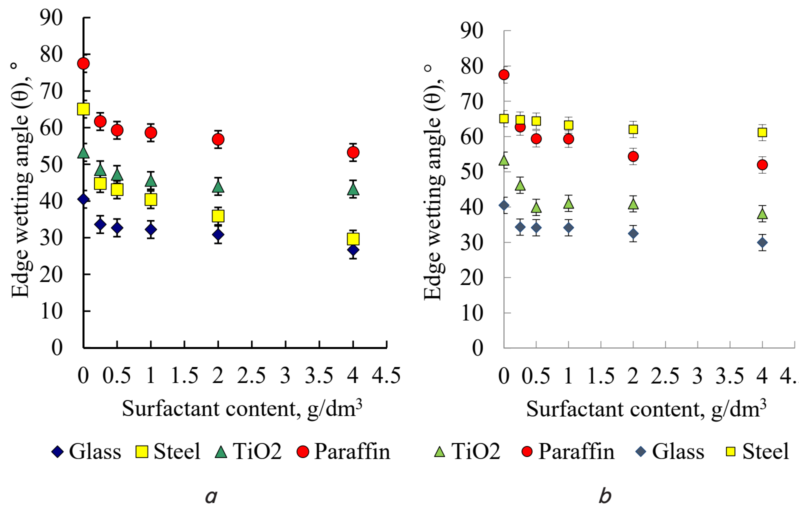


Fig. 6. Edge angles of wetting of hard surfaces with aqueous solutions of surfactants: *a* — polyether siloxane (PS); *b* — sodium polyacrylate (SPA)

The introduction of additives into the water causes a decrease in the edge wetting angle (θ°) on all the substrates examined.

5. 2. Studying the edge angle of wetting of substrates, in the presence of surfactants and an acrylic film-forming agent

The influence of PS on the edge angles of wetting of substrates is shown in Fig. 7.

The effect of SPA on the edge angles of wetting of substrates is shown in Fig. 8.

The introduction of PS into acrylic-containing compositions has an ambiguous effect on wetting the substrates. When using SPA, the edge wetting angles are reduced on all substrates.

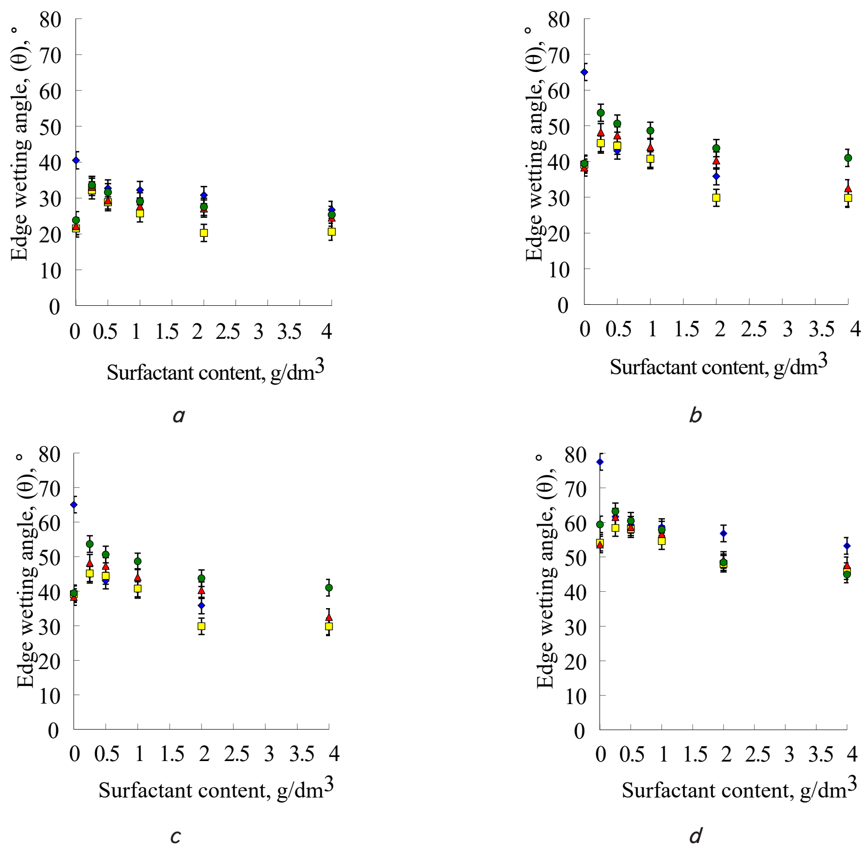


Fig. 7. Edge angles of wetting of hard surfaces with aqueous and acrylic-containing compositions in the presence of polyether siloxane (PS): *a* – glass; *b* – steel; *c* – titanium dioxide; *d* – paraffin; acrylic resin content in solution: ◆ – 0 %; ■ – 10 %; ▲ – 20 %; ● – 30 %

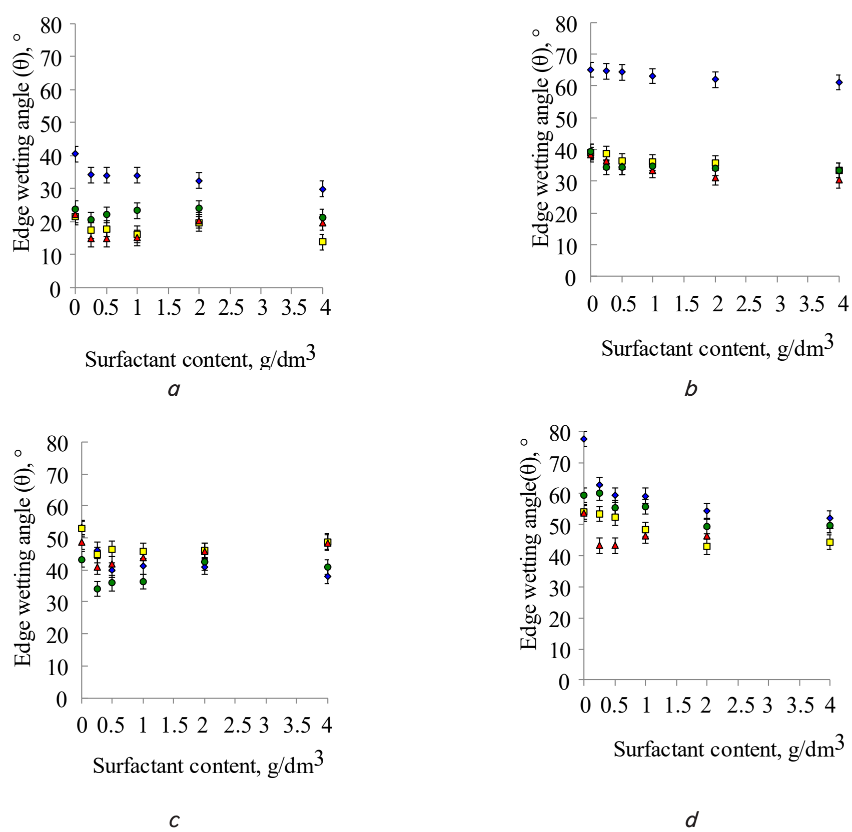


Fig. 8. Edge angles of wetting of hard surfaces with aqueous and acrylic-containing compositions in the presence of sodium polyacrylate (SPA): *a* – glass; *b* – steel; *c* – titanium dioxide; *d* – paraffin; acrylic resin content in solution: ◆ – 0 %; ■ – 10 %; ▲ – 20 %; ● – 30 %

5. 3. Studying the work of adhesion of an acrylic film-forming agent solution on a steel substrate

The influence of surfactants on the adhesion of industrial WB paints solutions (the content of an acrylic film-forming agent of 60 % by weight) to the steel substrate is shown in Fig. 9.

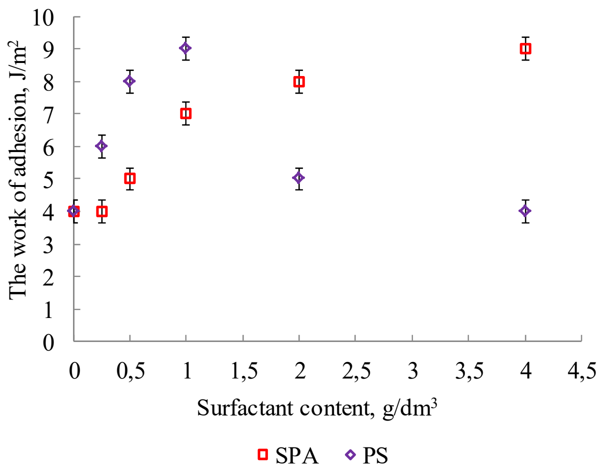


Fig. 9. Influence of surfactants on the adhesion of solutions of industrial acrylic paints (a film-forming agent's content of 60 % by weight) to the steel substrate

The introduction of surfactants into acrylic-containing compositions increases the adhesion of WB paints solutions on a steel substrate.

5. 4. Modeling the joint effect of the concentration of surfactants and a film-forming agent on the wetting ability of water-borne compositions

To derive a two-factor statistical mathematical model of the effect of surfactants and the content of an acrylic film-forming agent on the wettability of titanium dioxide, we used (1). The reliability of the obtained mathematical models was estimated by calculating the coefficient of nonlinear multiple correlation *R* (2).

For PS, the following equation (*R*=0.776) was built: where C_S is the surfactant content, g/dm³;

$$\cos\theta = \frac{(0.0255 \cdot C_S + 0.6413)\cdot(0.0002 \cdot C_{FFA}^2 - 0.0051 \cdot C_{FFA} + 0.6721)}{0.6742}, \quad (4)$$

C_{FFA} – the content of an acrylic film-forming agent, %.

For SPA, the following equation was built (*R*=0.818)

$$\cos\theta = \frac{\left(0.65 + 0.09\cdot\left(1-e^{-10C_S}\right)\right)\cdot(0.0003 \cdot C_{FFA}^2 - 0.0072 \cdot C_{FFA} + 0.7236)}{0.7215}, \quad (5)$$

where C_S is the surfactant content, g/dm³; C_{FFA} – the content of an acrylic film-forming agent, %.

To derive a two-factor statistical mathematical model of the effect of surfactants and the content of acrylic film-forming on the wettability of steel, we used (1). The reliability of the obtained mathematical models was estimated by calculating the coefficient of nonlinear multiple correlation *R* (2).

For PS, the following equation (*R*=0.648) was built:

$$\cos\theta = \frac{(0.042 \cdot C_S + 0.6783)\cdot(-0.0003 \cdot C_{FFA}^2 + 0.0075 \cdot C_{FFA} + 0.7218)}{0.7325}. \quad (6)$$

For SPA, the following equation was constructed (*R*=0.997)

$$\cos\theta = \frac{\left(0.69 + 0.06\cdot\left(1-e^{-1.3C_S}\right)\right)\cdot\left(0.45 + 0.37\cdot\left(1-e^{-0.3C_{FFA}}\right)\right)}{0.7241}, \quad (7)$$

where cos θ is the cosine of the edge angle of wetting; C_{FFA} is the content of an acrylic film-forming agent, %; C_S is the concentration of surfactants in the solution, g/dm^3.

Using the Student's criterion, the significance of all coefficients of nonlinear multiple correlation calculated from (2) was established. Thus, all the resulting approximation equations are reliable.

The obtained two-factor statistical mathematical models can be used to search for optimal concentrations of surfactants and an acrylic film-forming agent, providing the maximum wetting ability of water-borne compositions in relation to titanium dioxide and steel. In addition, these models can be used to build nomograms.

5. 5. Studying the effect of surfactants on the anti-corrosion characteristics of coatings

The effect of surfactants on the corrosion rate in distilled water is shown in Fig. 10. To assess the effect of surfactants on the resistance of acrylic coatings to the effects of salt spray, we studied corrosion rate in 60 % NaCl solution, shown in Fig. 11.

To assess the effect of surfactants on the decorative characteristics of acrylic enamel, the gloss of coatings was investigated. The effect of surfactants on the gloss of coatings is shown in Fig. 12.

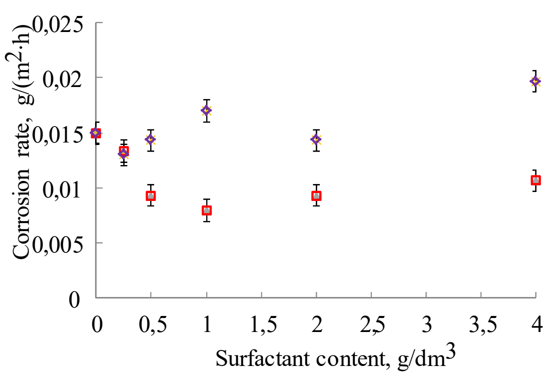


Fig. 10. Effect of surfactant content on the corrosion rate of steel substrate protected by acrylic coating in distilled water (within 30 minutes and temperature (25±2) °C)

The effect of surfactants on the adhesion of the coating is shown in Fig. 13.

The effect of surfactants on the appearance of the coating is shown in Fig. 14.

Fig. 14 shows that the introduction of surfactants into acrylic compositions improves the appearance of the coating (reduces the roughness of the films).

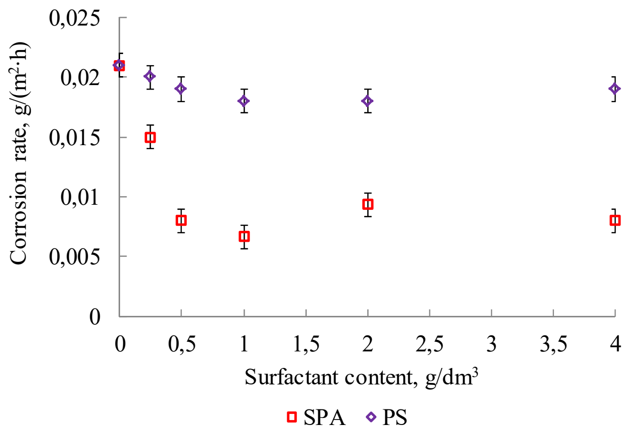


Fig. 11. Influence of surfactant content on the corrosion rate of steel substrate protected by acrylic coating in 60 % NaCl solution (within 30 minutes and temperature (25±2) °C)

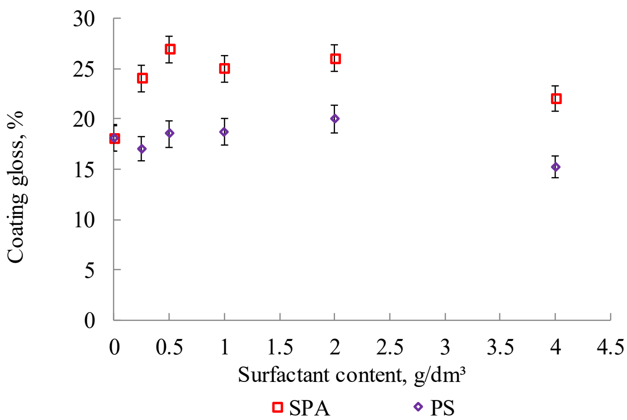


Fig. 12. Effect of surfactant content on the gloss of acrylic coatings

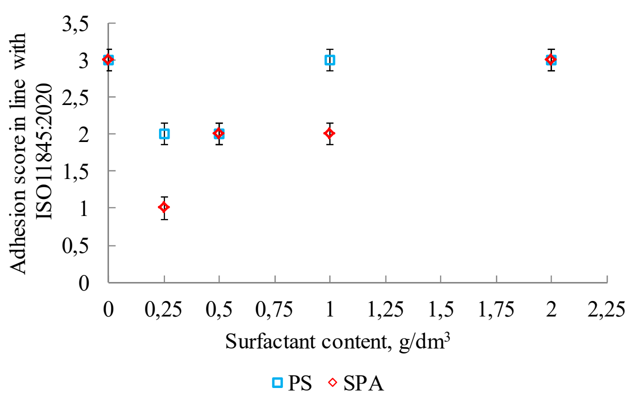


Fig. 13. Effect of surfactant content on the adhesion of acrylic coatings

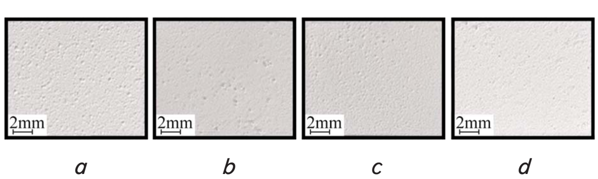


Fig. 14. The effect of the content of surfactants on the appearance of the acrylic coating: *a* – without surfactants; *b* – with PS 1 g/dm^3; *c* – with SPA 1 g/dm^3; *d* – with PS 4 g/dm^3

6. Discussion of results of the substrate wetting study

According to Fig. 6, the wetting activity of the surfactant can be delimited into two areas. The first region includes a concentration area of 0 to 0.25 g/dm^3, the second – exceeding 0.25 g/dm^3. Analysis of the results obtained at the first site shows that in the absence of surfactants in water (C_S=0 g/dm^3), the surfaces for reducing hydrophilicity form a series: glass (Δθ=40.50°)>titanium dioxide (Δθ=53.27°)>steel (Δθ=65.05°)>paraffin (Δθ=77.49°), that is, water wets the glass best.

Experimental data indicate that the introduction of surfactants into water stimulates the development of wetting processes, the features of which are determined by the nature of the surface and the concentration of the surfactant. Due to the maximum decrease in the edge angle of wetting on the test substrates on the initial (C_S≤0.25 g/dm^3) section of isotherms and to compare the wetting activity of PS $\left(\frac{d\cos\theta}{dC_S}\right)_{C_S\to 0}$ on the substrates under study, these areas were approximated by an equation of the following form:

$$\cos\theta=\cos\theta_0+Z\cdot C_S, \tag{8}$$

where $\cos\theta_0$ is the cosine of the angle formed by water in the absence of surfactants;

Z is a constant.

After differentiating equation (8), the following was obtained:

$$\frac{d\cos\theta}{dC_S}=Z. \tag{9}$$

The corresponding Z values are given in Table 4.

Table 4

Coefficients in equation 9

Surfactant	substrate	steel	paraffin	glass	ilmenite
PS	$d\cos\theta/dC_S$	1.15	1.03	0.29	0.26
SPA	$d\cos\theta/dC_S$	0.02	0.97	0.26	0.38

As follows from the analysis of the data obtained, the maximum wetting activity of PS is shown in relation to steel (Z=1.15) and the minimum (Z=0.26) – on titanium dioxide. It is interesting to compare the intermediate values of the wetting activity of PS on paraffin (Z=1.03) and glass (Z=0.29).

In the reference literature, data are given that paraffin has a significantly lower dielectric constant (ε=2.2) than glass (ε=5÷9) and even more so water (ε=81). It is for this reason that polar water better wets the polar surface of glass (θ=40.50°) than paraffin (θ=77.49°).

The PS introduced into the water demonstrates 3.55 times greater wetting activity on paraffin than glass, which is quite understandable from the Rehbinder equation rule. The surface activity of PS is greater, the greater the difference in polarities (ε), contacting phases, and it is greater between paraffin and water. The same patterns with respect to these two diametrically opposed surfaces persisted for SPA (Fig. 8). The values of the wetting activity of SPA on paraffin (z=0.97) and glass (z=0.26) were very close to PS. However, this indicator for SPA in relation to the steel surface is much less (z=0.02) and slightly more in titanium dioxide (z=0.38) than for PS (Fig. 7).

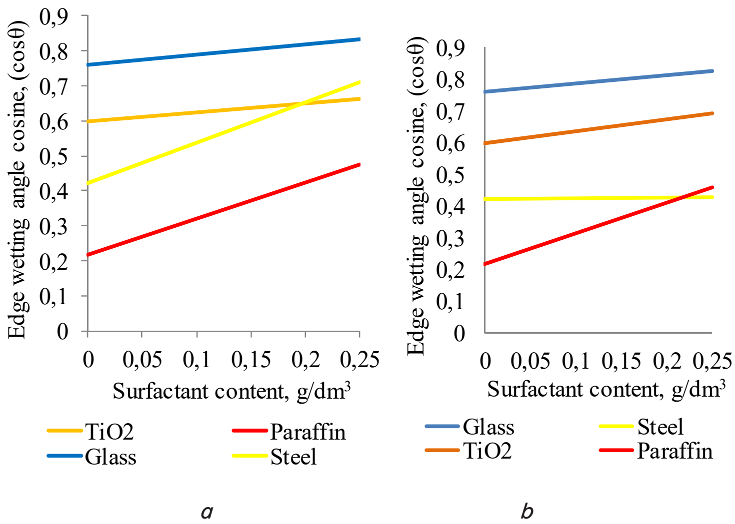


Fig. 15. The dependence of the cosine of the edge angle of wetting of a solid surface on the concentration: *a* – polyether siloxane; *b* – sodium polyacrylate

With the subsequent dosing of surfactants (C_S>0.25 g/dm^3), a deviation of the dependences θ=*f*(C_S) from rectilinearity was noted (section II, Fig. 6, *a*, *b*). The decrease in the increase in the hydrophilicity of PS solutions at the second concentration site in relation to the studied surfaces was different. On the steel plate, the edge angle further changed by 15.10° with an increase in the concentration of PS from 0.25 to 4 g/dm^3 and became close in value (θ=29.60°) to the wetting index of the hydrophilic surface of the glass itself (θ=26.67°).

Within the same concentration limits of injected PS, the decrease in θ on the surface of paraffin, glass, and titanium dioxide was not as significant (8.43°, 6.93°, and 5.28°, respectively). In SPA solutions at a concentration range of 0.25 to 4 g/dm^3, the θ value was further changed on the steel surface from 64.68° to 61.10°, on titanium dioxide from 46.18° to 38.10°, on glass from 34.31° to 29.94°, on paraffin from 62.70° to 51.94°.

If we consider the entire area of the studied concentrations of surfactants (from 0 to 4 g/dm^3), then the maximum increase in the wettability for SPA (Δθ=25.54°) occurs on the surface of paraffin, for PS – on a steel surface (Δθ=35.46°). It should be noted that the achievement of such a high degree of reduction in surface energy at the water-solid boundary under the influence of additives significantly exceeds the surface activity of surfactants in organic media, as evidenced by numerous studies in this area [18–20].

As evidenced by experimental data, the introduction of 10 % film-forming agent into water in the absence of additives (C_S=0 g/dm^3) is accompanied by a decrease in the edge angle of wetting.

Surfaces to reduce hydrophilicity form a series: steel (Δθ=25.90°)>paraffin (Δθ=23.33°)>glass (Δθ=18.99°)>titanium dioxide (Δθ=0.50°), that is, polyacrylates best wet steel. A further increase in the content of a film-forming agent (C_{FFA}>10 %) in water slightly affected changes in the edge angle of wetting. This feature was also noted in organ-dilute compositions [21], that is, regardless of the nature of the solvent, an increase in the concentration of a high-molecular film-forming agent contributes to the association of its macromolecules and, as a consequence, a decrease in its surface activity.

As regards the influence of additives in water-borne compositions, PS (Fig. 7) and SPA (Fig. 8) in such systems demonstrate pronounced differences in wetting activity. Polyether siloxane, in a situation where access to the active centers of the solid surface in the presence of a film-forming agent is different, shows an inversion in the wetting indicators with C_S≤0.25 g/dm^3. With respect to all types of solid surface, the values of θ increased (Fig. 7, *a–d*), while in water at the same concentration interval the maximum wetting effect of PS was manifested (Fig. 6, *a*). The increase in the edge angle (relative to unmodified compositions with different film-forming contents) occurred most intensively on steel (Δθ=6.02°÷14.24°) and glass (Δθ=9.82°÷10.93°). The hydrophobic effect of PS was less on the surface of paraffin (Δθ=3.76°÷7.91°) and titanium dioxide (Δθ=2.39°÷4.89°). However, outside the concentration area (C_S>0.25 g/dm^3), the wetting effect of surfactants changed dramatically. The edge angle of wetting began to gradually decrease and, at C_S=4 g/dm^3, the θ values were approximately at the same level as in compositions without PS (Fig. 7, *a–d*).

Unlike PS, when SPA is introduced into acrylic-containing compositions, the inversion in indicators of θ is not established (Fig. 8). In the presence of a film-forming agent, the wetting effect of SPA is enhanced on the steel surface (Fig. 9, *a*). With an increase in the concentration of surfactants from 0 to 4 g/dm^3, the decrease in θ values was in the range of 7.95°÷5.73°, while in water it was only 3.01°. On the remaining three surfaces, the extreme nature of the change in the wetting activity of SPA was noted. On non-polar paraffin, the minimum edge angle of wetting was recorded at a concentration of sodium polyacrylate 2 g/dm^3, on more polar surfaces of glass and titanium dioxide (Fig. 8, *b–d*) extremes shifted to the region of lower values (C_S=0.25 g/dm^3). The decrease in the values of θ on paraffin with an increase in concentration from 0 to 2 g/dm^3 was 10.07°÷11.50°, which is almost two times less than its effect in water (Fig. 8, *d*). On glass, the difference in the wetting effect of SPA between acrylic-containing compositions (3.34°÷7.30°) and water (10.75°) at the concentration point of the extremum (C_S=0.25 g/dm^3) is less significant and on the surface of titanium dioxide it is practically equalized: 9.23°÷7.68° (Fig. 8, *c*) and 7.08° (Fig. 8, *c*).

Using the PDP method, approximation equations (two-factor statistical mathematical models) were built, taking into consideration the influence of factors such as the concentration of surfactants and the concentration of acrylic film-forming agents on the process of wetting titanium dioxide and steel. These models can be used to determine the optimal compositions of water-borne compositions that provide maximum wetting of the surface of the pigment and steel substrate. For the process of wetting the steel surface and pigment, nomograms have been constructed (Fig. 16, 17) to find the required concentration of surfactants for the specified values of cosθ depending on the content of the acrylic film-forming agent in the paint composition.

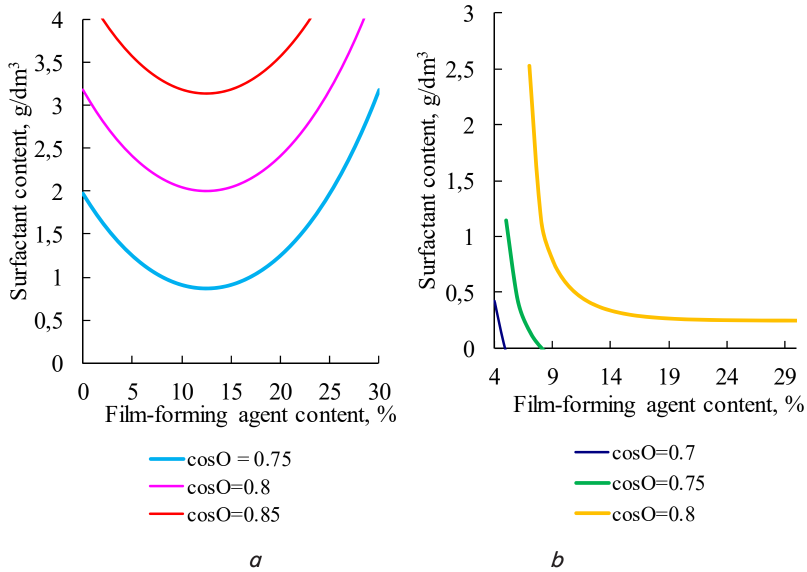


Fig. 16. Nomograms C_S=*f*(cosθ, C_{FFA}) for wetting the surface of steel: *a* – polyether siloxane (PS); *b* – sodium polyacrylate (SPA)

The introduction of SPA (Fig. 10) into paints significantly reduces the corrosion rate of coatings in distilled water, by 45 %. For PS, this effect has not been recorded. In addition, the introduction of surfactants (Fig. 11) also reduces the corrosion rate of coatings in a 60 % NaCl solution. For SPA, this decrease is 60 %, and for PS only 10...12 %. An interesting effect of surfactants on the gloss of acrylic coatings was revealed (Fig. 12). As the content of SPA in the coatings increased, the gloss increased by almost 50 % (from 18.1 to 26.9 %). For coatings with PS, a slight increase in gloss was registered. The introduction of SPA (Fig. 13) in the composition significantly improves the adhesion of coatings (from 3 to 1 point). This fully correlates with the growth of the adhesion of WB paints solutions on a steel substrate. The additive that most increases the wetting work and adhesion of the coating is sodium polyacrylate (SPA):

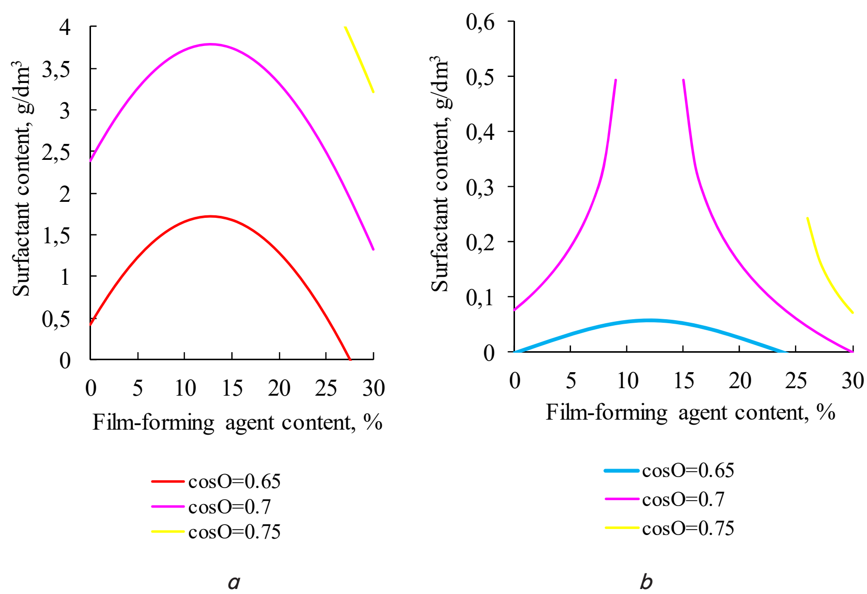


Fig. 17. Nomograms C_S=*f*(cosθ, C_{FFA}) for wetting the surface of titanium dioxide: *a* – polyether siloxane (PS); *b* – sodium polyacrylate (SPA)

Consequently, there is a close correlation between the wetting activity of surfactants and the protective (anti-corrosion) and decorative properties of acrylic coatings. SPA is characterized by the maximum increase in wetting of the steel substrate (relative to PS) and at the same time, the maximum protective characteristics of the coatings (minimum corrosion rate in water and NaCl solution) and maximum gloss are recorded.

This study was carried out strictly at a constant temperature (20±2) °C. However, under actual industrial conditions (in the process of applying such paints), the temperature in the painting areas cannot always be in the range from 18 to 22 °C. In the paint/painting shops, more significant te perature fluctuations are observed (from –2 to +35 °C). When the temperature changes, the fluctuations of the edge angles of wetting and surface tension of acrylic paint solutions can significantly change the operation of adhesion.

A logical continuation of this study is to investigate the influence of the considered additives on the physical and mechanical properties of coatings. It would be interesting to trace the effect of improving the wetting of pigment and steel substrate on impact resistance, wear resistance, and hardness of coatings. In addition, it would be interesting to study the effect of improving pigment wetting on the aggregate stability of its suspensions.

7. Conclusions

1. In aqueous solutions of surfactants, polyether siloxane exhibits maximum wetting activity against steel ($dCos\theta/dC_S$=1.15) and minimum wetting activity against titanium dioxide ($dCos\theta/dC_S$=0.26). Sodium polyacrylate in relation to the steel surface shows significantly less wetting activity ($dCos\theta/dC_S$=0.02) and greater ($dCos\theta/dC_S$=0.38) on titanium dioxide, in comparison with polyether siloxane. The wetting activity of sodium polyacrylate and polyether siloxane are close in their values on paraffin ($dCos\theta/dC_S$=0.97–1.03) and glass ($dCos\theta/dC_S$=0.26–0.29).

2. In acrylic-containing compositions, the wetting effect of sodium polyacrylate relative to the steel surface is enhanced in comparison with the aqueous solution of surfactants. With an increase in the concentration of SPA from 0 to 4 g/dm^3, the decrease in the values of the edge angle of wetting was 7.95÷5.73°, while in water – 3.01°. In relation to titanium dioxide, the wetting activity of SPA does not depend on the content of the film-forming agent in the water. The decrease in θ values with an increase in the concentration of SPA from 0 to 0.25 g/dm^3 is 7.08° in water and

7.68°÷9.23 in acrylic-containing compositions. The contribution of polyether siloxane to the development of wetting processes decreases in the presence of a film-forming agent, which is confirmed by an increase in the edge wetting angles at the concentration site from 0 to 0.25 g/dm^3. The subsequent decrease in θ with an increase in the concentration of PS from 0.25 to 4 g/dm^3 makes it possible only to approach the level of unmodified compositions, regardless of the nature of the solid surface.

3. The introduction of surfactants into acrylic-containing compositions increases the adhesion of WB paints solutions on a steel substrate. For SPA and PS, the maximum increase in adhesion is 125 %.

4. Based on the method of probabilistic-deterministic planning, equations for calculating the edge wetting angle of titanium dioxide and steel depending on the content of the film-forming and surfactant have been built.

5. The introduction of surfactants in the compositions improves the anti-corrosion and decorative properties of coatings. The most effective additive to acrylic paint is SPA. With optimal SPA contents in the compositions, the corrosion rate of coatings is reduced (in distilled water by 45 % in NaCl solution by 60 %). At the same time, the gloss increases by 50 %, adhesion by 2 points (according to ISO 11845:2020). This fully correlates with the nature of the effect of surfactants on the wetting of the steel substrate and pigment (titanium dioxide).

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References

1. Ortiz-Herrero, L., Cardaba, I., Bartolomé, L., Alonso, M. L., Maguregui, M. I. (2020). Extension study of a statistical age prediction model for acrylic paints. Polymer Degradation and Stability, 179, 109263. doi: https://doi.org/10.1016/j.polymdegradstab.2020.109263
2. Dao, P. H., Nguyen, T. D., Nguyen, T. C., Nguyen, A. H., Mac, V. P., Tran, H. T. et. al. (2022). Assessment of some characteristics, properties of a novel waterborne acrylic coating incorporated TiO2 nanoparticles modified with silane coupling agent and Ag/Zn zeolite. Progress in Organic Coatings, 163, 106641. doi: https://doi.org/10.1016/j.porgcoat.2021.106641
3. Kozakiewicz, J., Trzaskowska, J., Domanowski, W., Kieplin, A., Ofat-Kawalec, I., Przybylski, J. et. al. (2020). Studies on synthesis and characterization of aqueous hybrid silicone-acrylic and acrylic-silicone dispersions and coatings. Part II. Progress in Organic Coatings, 138, 105297. doi: https://doi.org/10.1016/j.porgcoat.2019.105297
4. Ji, S., Gui, H., Guan, G., Zhou, M., Guo, Q., Tan, M. Y. J. (2021). A multi-functional coating based on acrylic copolymer modified with PDMS through copolymerization. Progress in Organic Coatings, 156, 106254. doi: https://doi.org/10.1016/j.porgcoat.2021.106254
5. Ji, S., Gui, H., Guan, G., Zhou, M., Guo, Q., Tan, M. Y. J. (2021). Molecular design and copolymerization to enhance the anti-corrosion performance of waterborne acrylic coatings. Progress in Organic Coatings, 153, 106140. doi: https://doi.org/10.1016/j.porgcoat.2021.106140
6. Voogt, B., Venema, P., Sagis, L., Huinink, H., Erich, B., Scheerder, J., Adan, O. (2019). Surface characterization of drying acrylic latex dispersions with variable methacrylic acid content using surface dilatational rheology. Journal of Colloid and Interface Science, 556, 584–591. doi: https://doi.org/10.1016/j.jcis.2019.08.074
7. Arai, K., Mizutani, T., Kimura, Y., Miyamoto, M. (2016). Unique structure and properties of inorganic–organic hybrid films prepared from acryl/silica nano-composite emulsions. Progress in Organic Coatings, 93, 109–117. doi: https://doi.org/10.1016/j.porgcoat.2015.12.002
8. Zhou, G. qiang, Wang, Y. Y. (2019). Preparation and application of modified hydr oxyl acrylic dispersion without solvent by a four step synthetic approach. Progress in Organic Coatings, 130, 93–98. doi: https://doi.org/10.1016/j.porgcoat.2019.01.049
9. Wong, J. C., Ngoi, K. H., Chia, C. H., Jeon, T., Kim, H., Kim, H.-J. et. al. (2022). Surface hardness and abrasion resistance natures of thermoplastic polymer covers and windows and their enhancements with curable tetraacrylate coating. Polymer, 239, 124419. doi: https://doi.org/10.1016/j.polymer.2021.124419
10. Silva, M. F., Doménech-Carbó, M. T., Osete-Cortina, L. (2015). Characterization of additives of PVAc and acrylic waterborne dispersions and paints by analytical pyrolysis–GC–MS and pyrolysis–silylation–GC–MS. Journal of Analytical and Applied Pyrolysis, 113, 606–620. doi: https://doi.org/10.1016/j.jaap.2015.04.011
11. Izmitli, A., Ngunjiri, J., Lan, T., Pacholski, M. L., Smith, R., Langille, M. et. al. (2019). Impact of silicone additives on slip/mar performance and surface characteristics of waterborne acrylic coatings. Progress in Organic Coatings, 131, 145–151. doi: https://doi.org/10.1016/j.porgcoat.2019.02.019
12. Bamane, P. B., Jagtap, R. N. (2022). Synthesis and characterisation of a non-halogenated water-based functional additive to improve ink-adhesion on untreated polypropylene surfaces. International Journal of Adhesion and Adhesives, 113, 103077. doi: https://doi.org/10.1016/j.ijadhadh.2021.103077
13. Ouyang, S., Lin, Z., Cao, L., Ding, Y., Shen, L. (2021). Preparation of excellent-water-resistance water-borne alkyd/acrylic hybrid coatings with varied maleic anhydride content. Progress in Organic Coatings, 161, 106537. doi: https://doi.org/10.1016/j.porgcoat.2021.106537
14. Kubiak, K. J., Mathia, T. G., Wilson, M. C. T. (2009). Methodology for metrology of wettability versus roughness of engineering surfaces. Proceeding of 14th International Congress of Metrology. Available at: https://www.researchgate.net/publication/215751897_Methodology_for_metrology_of_wettability_versus_roughness_of_engineering_surfaces

15. Malyshev, V. P. (1981). Veroyatnostno-determinirovannoe planirovanie eksperimenta. Alma-Ata: Nauka AN KazSSR, 116. Available at: https://rusneb.ru/catalog/000199_000009_001059848/
16. Ostrovnoy, K., Dyuryagina, A., Demyanenko, A., Tyukanko, V. (2021). Optimization of titanium dioxide wetting in alkyd paint and varnish materials in the presence of surfactants. Eastern-European Journal of Enterprise Technologies, 4 (6 (112)), 41–50. doi: https://doi.org/10.15587/1729-4061.2021.237879
17. Protod'yakonov, M. M. (1932). Sostavlenie gornyh norm i pol'zovanie imi. Moskva, Leningrad, Novosibirsk: Gos. Nauchno-tekhn. Gornoe izd-vo, 36. Available at: https://rusneb.ru/catalog/000200_000018_rc_2676489/
18. Dyuryagina, A. N., Tyukan'ko, V. Yu., Demyanenko, A. V., Kukemin, Ye. A. (2010). Study of polyorganosiloxanes wetting activity in the presence of surfactants. Lakokrasochnye materialy i ih primenenie, 10, 38–40. Available at: https://www.elibrary.ru/item.asp?id=23487903
19. Dyuryagina, A. N., Kulemina, E. A., Poluykova, A. A., Degtyareva, S. I. (2012). Issledovanie smachivayuschey sposobnosti aminosoderzhaschih poverhnostno-aktivnyh veschestv. Himicheskiy zhurnal Kazahstana, 1, 128–135. Available at: https://nauka.kz/page.php?page_id=964&lang=1&page=4586
20. Tyukanko, V. Y., Duryagina, A. N., Ostrovnoy, K. A., Demyanenko, A. V. (2017). Study of wetting of aluminum and steel substrates with polyorganosiloxanes in the presence of nitrogen-containing surfactants. Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering, 328 (11), 75–82. Available at: http://izvestiya.tpu.ru/archive/article/view/1949
21. Dyuryagina, A. N., Ostrovnoy, K. A., Kozik, D. Yu. (2021). Modifying effect of petrochemical waste processing products on wetting and stabilization of solid-phase particles. Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering, 332 (12), 164–172. doi: https://doi.org/10.18799/24131830/2021/12/3124