

This paper reports the results of studying the influence of surfactants (SAS) on the wetting of titanium dioxide in alkyd paint and varnish materials (PVM), based on pentaphthalic (PPh) and alkyd-urethane (AU) film-forming substances. Edge wetting angle (θ°) and adhesion work (Wa) were used as the criteria for assessing the wettability of titanium dioxide. Three additives were used as SAS: the original product AS-1, obtained from waste of oil refining (with low cost), and industrial additives: "Telaz" and polyethylene polyamine (PEPA). All the studied additives in PPh and AU PVM improve the wetting of titanium dioxide. At the 30 % content of AS film-forming substance in the composition, the maximum decrease in θ° for AS-1 is 4.5°, for PEPA and Telaz it is 4°. For pentaphthalic composition under similar conditions, a decrease in edge wetting angle for AS-1 is 10°, for Telaz 8.6°, and for PEPA 5.9°. According to the relative change in edge wetting angle for both systems, the maximum decrease in θ° is about 10 %. The introduction of SAS into the composition of AU ambiguously affects the adhesion work, for PPh, the introduction of SAS causes a decrease in adhesion work (Wa). AS-1 is the SAS that minimally reduces adhesion work. The compositions of the PVM by the method of probabilistic-deterministic planning, which ensures maximum wetting of titanium dioxide with film-forming solutions, were analyzed. The equations for calculating the edge angle of wetting of titanium dioxide depending on the content of solvent and the SAS in the PVM were derived. The effectiveness of the AS-1 product as a wetting additive for alkyd paints and varnishes was proven. The wetting ability of the original SAS – AS-1 is close to industrial additives PEPA and Telaz

Keywords: wetting, surfactant, titanium dioxide, pigment, alkyd enamels, adhesion work

OPTIMIZATION OF TITANIUM DIOXIDE WETTING IN ALKYD PAINT AND VARNISH MATERIALS IN THE PRESENCE OF SURFACTANTS

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1. Introduction

Alkyd paints and varnishes (hereinafter PVM) historically occupy a significant share of the market of anti-corrosion coatings used for painting products in mechanical engineering. One of the main reasons for their prevalence and demand in the industry is a low price. Among the wide palette of alkyd film-forming substances: glyphthalic, pentaphthalic, alkyd-urea-formaldehyde, alkyd-acrylic, alkyd-urethane, and alkyd-styrene, pentaphthalic and glyphthalic are currently most common. For 70 years, the coating system (hereinafter PVC), consisting of the first layer of primer GF-021 and two subsequent layers of enamel PF-115 has proven itself well in mechanical engineering. It provides a protective life of the PVC for at least 5 years in the operating conditions of UHL1/outdoors/according to GOST 15150-69. However, in mechanical engineering, there is a tendency to increase the use of alkyd-urethane paints and varnishes [1]. This is due to the fact that they provide more oil-, gasoline-resistant, hard and wear-resistant coatings than pentaphthalic coatings. For mechanical engineering, the determining factor in their application is a much greater protective resource of paint and varnish coatings formed by them (up to 10 years) in contrast to pentaphthalic coatings.

A significant increase in the quality of alkyd coatings, achieved over the past 50 years, is explained by the widespread use of broad-spectrum additives by manufacturers of coatings (Germany (Dispex (BASF), Germany Additol (Allnex), USA Orotan (Dow Chemical), Germany Hydropalat (Cognis), USA Nuosperse (Servo), Russia LLC NPP "AVTOCONINVEST", NEO Chemical and Eurosynthesis). However, they have a fairly high cost. Due to the deteriorating economic situation caused by the COVID-19 coronavirus pandemic, the development of cheap additives derived from chemical waste is becoming relevant.

The original industrial product obtained from oil refining waste AS-1 was used in the study as an additive, the synthesis of this product was carried out in the laboratory of the Kozybayev Central Agricultural Institute of Agriculture, Petropavlovsk, North Kazakhstan, Kazakhstan [2].

In addition, to compare the assessment of the effect of AS-1 on wetting of pigment relative to the additives produced on an industrial scale, the study used additional additives: "Dispersant Telaz D" and PEPA.

The relevance of scientific problems is due to the need to study the wettability of pigments with solutions of film-forming substances in the composition of PVM and the effect of surfactant additives on these processes. The results

of these studies are important for modern industry, as they would make it possible to create new anti-corrosion alkyd paint and varnish materials, with increased service life. These paints and coatings could well be used in mechanical engineering for painting various parts, nodes of machines and mechanisms.

2. Literature review and problem statement

For the effective use of additives in specific PVM, it is necessary to conduct in-depth research in the field of colloidal chemistry and physical and chemical mechanics, rather than only use recommendations of manufacturers with “estimated consumption of additives”. For example, paper [3] presented a large number of industrial additives for PVM with the widest technological effect from dispersants and wetting agents to defoamers.

However, all the information in this source about their use and the optimal content of additives in the PVM are purely empirical in nature. Currently, there is no generally accepted “unified scientific theory of selection of additives” for various PVM, depending on the polarity of a polymer and a solvent, their solubility parameters, surface properties of pigments and fillers, etc.

That is why it was shown in paper [4] that the use of additives in the PVM has a large number of “pitfalls”.

Firstly, some additives are effective in certain PVM, while in others they are just useless (or even harmful). Secondly, the use of additives often leads to undesirable effects, especially if they are used in concentrations exceeding the optimal. In particular, surfactants are introduced into the PVM to facilitate wetting of the pigment surface but it leads to foam formation, which is corrected by another additive (silicone solution). Paper [5] shows that the duration of the protective life of the PVC is determined by: the size of pigment particles, its supramolecular structure, and the type of used alkyd resins, and all these parameters are regulated by the content of surfactants (hereinafter SAS) in the PVM. Article [6] provides a complete analysis of the use of SAS in PVM during the entire period of human development, from ancient times to the present day, the authors focus on the physical and chemical foundations of the use of the SAS in composite materials, including the PVM. The influence of the type and concentration of the SAS on the change of interphase energy and the stability of dispersed systems was shown. It is proved that the SAS in enamels and paints improve the aggregative and sedimentation resistance of suspensions/ dispersions. This is very relevant for the PVM. However, there is no answer to the question of the reasons for improving this resistance. Research [7] shows that in various PVM, the introduction of the SAS makes it possible to obtain coatings with the most uniform distribution of pigment particles in the polymer matrix, due to the maximum stability of suspensions “film-forming-pigment-SAS”. Moreover, for these coatings, the maximum properties are observed: protective resource, optical properties (for example, color), shine, coverability, and other characteristics. Study [8] showed that the introduction of the SAS in PVM causes an increase in the number of adhesive contacts “coating/pigment” and “coating/substrate”, as a result, the protective resource of the PVM increases. Article [9] deals in detail with the mechanism of improvement of stability of suspensions of PVM in the presence of SAS. It was shown that the improvement in

the resistance of suspensions “pigment – film-forming substance” is explained by the improved dispersion of pigment particles in a film-forming solution. In this case, a significant role is played by the improvement of the wetting of the pigment surface in the composition of the PVM with the solution of a film-forming substance. However, this paper does not propose any quantitative criteria for assessing the wettability of pigments. With the introduction of the SAS, the surface energy at the interphase boundary “film-forming solution/solid pigment surface” and “film-forming solution/solid substrate surface” decreases [10], which leads to an increase in wetting particles of pigments and substrate with the solution of the film-forming substance. However, in this work, no criteria for assessing the wettability of pigments are proposed either. In research [11], it is proved that for quantitative assessment of a change in wetting of pigment with a solution of a film-forming substance, it is expedient to use the estimated value – adhesion work. In addition, the positive side of this research is the improvement of wetting of titanium dioxide with film-forming solutions (reducing the edge wetting angle) at an increase in adhesion work. At the same time, the work did not study the effect of the SAS on adhesion work, the authors did not study the effect of additives on changing the surface properties of solutions.

In addition, vegetable oils used to produce alkyd film-forming substances are biodegradable compounds, which is currently the defining stimulus to study these materials. In paper [12], an exhaustive review of vegetable oils currently used and potentially possible for use in the PVM was performed. The review highlights the impact on some modern PVM modifications, such as environmentally friendly coatings with low content of solvent or its absence, with a high content of particulate matter, hyperbranched, water-diluted, and UV-curable PVC. However, in this review, there is no information on changes in the legislation of leading countries in the field of manufacture and use of the PVM. In paper [13], this point is considered in detail, namely, amendments to the “Clean Air Act”, USA. The amendments require that industry should reduce emissions of volatile organic compounds, which contribute to the ozone decomposition in the lower atmosphere.

Currently, there is no generally accepted theory of the choice of the type and concentration of additives-wetting agents in the PVM (depending on the chemical composition, molecular weight, or other parameters), there are no general criteria for assessing the wettability of pigments and fillers, there is no information about the study of wettability of pigments with film-forming solutions based on alkyd resins. All these issues need to be addressed.

3. The aim and objectives of the study

The purpose of this study is to optimize the wetting of titanium dioxide with solutions of alkyd film-forming substances by regulating the content of surfactants and solvents in the PVM, with the construction of a mathematical model of the process. This will make it possible to obtain pentaphthalic and alkyd-urethane PVM with the maximum possible protective, decorative, and structural-mechanical characteristics of their coatings.

To achieve the aim, the following tasks were set:

- to study the influence of the content of the SAS and the solvent on the wetting of titanium dioxide in pentaphthalic and alkyd-urethane paint and varnish materials;

– to study the influence of the SAS and solvent content on adhesion work (W_a) of pentaphthalic and alkyd-urethane film-forming solutions on titanium dioxide;

– to optimize the compositions of alkyd paint and varnish materials, ensuring maximum wetting of titanium dioxide with film-forming solutions;

– to prove or disprove the effectiveness of the product AS-1 as a wetting additive for alkyd paint and varnish materials.

4. Materials and methods of research

The following were used as film-forming substances:

1) Alkyd-urethane varnish "Uralkyd" (TU 2311-023-45822449-2002). It is a solution of pentaphthalic resin in white spirit modified with fatty acids of tall oil and toluene diisocyanate. Conditional viscosity of varnish (at a temperature of 20 °C according to the viscometer VZ-246 with a nozzle diameter of 4 mm), is 200–260; mass fraction of non-volatile substances, % – 49). Varnish manufacturer – LLC "Tsvetnoy Boulevard", Omsk, Russia.

The structure of the alkyd-urethane film-forming substance is shown in Fig. 1.

2) Pentaphthalic varnish PF-060 according to TU 2311-041-56041689-2006.

Pigment titanium dioxide of the R-02 brand (GOST 9804-84) of rutile form (mass fraction of titanium dioxide of rutile form is 95 %) manufactured by PJSC "Crimean TITAN", Ukraine, was used as a substrate.

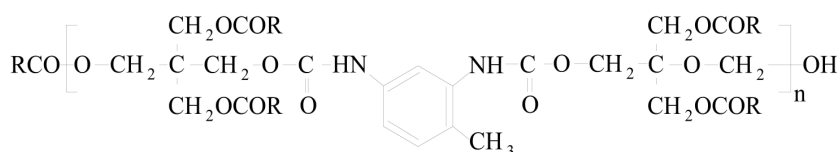
The following was used as SAS/additives-wetting agents:

1) The original SAS was obtained from oil refining waste – a mixture of primary and secondary amines AS-1 (molecular weight – 250 a.e.m.; amine number (mg/g) – 30) [2].

2) Technical product of the condensation of vegetable oils with diamines under the trademark "Dispersant Telaz D" (molecular weight 2121 a.e.m.; amine number (mg NCI/g) – 32) manufactured by Avtokoninvest, Russia.

3) Technical product, a mixture of high-molecular amines PEPA (molecular weight 4,950 a.e.m.; amine number (mg NCI/g) – 31), manufactured by JSV "Ural-ChemPlast", Russia.

The structures of alkyd-urethane film-forming substance and SAS/additives-wetting agents are shown in Fig. 1.



Alkyd-urethane film-forming substance

$R'-NH_2$ and $R'-NH-R''$,
where R' - n-butyl; R'' - 2-ethyl-2-hexenyl (in ratio of 1:3)
(AS-1)

$(-CH_2-CH(NH_2))_n$
 $n = 45 \div 50$
(Telaz)

$(-C_2H_4-NH-C_2H_4-NH-)_n$
 $n = 55 \div 60$
(PEPA)

White spirit (GOST 3134-78) was used as a solvent. White spirit is a mixture of liquid aliphatic and aromatic hydrocarbons obtained by direct distillation of oil. The density of white spirit is 0.790 g/cm³ (at 20 °C), the mass fraction of aromatic hydrocarbons is not more than 16 %. The manufacturer of white spirit is LLP "Fund-2", Kazakhstan.

Given a large number of concentrations of the SAS and the solvent under study, the experiments were planned using the method of probabilistic-deterministic planning (hereinafter PDP). The PDP method determines the best combination of input data for the production of composite with specified properties [14]. At the first stage, an experiment plan was formed using the method of probabilistic-deterministic planning. This method involves the formation of an experiment matrix plan that meets two requirements:

1) all possible combinations of levels of any two input parameters should be presented in the plan of the experiment, i. e. any level of one of the given arbitrarily selected pair of parameters corresponds to all levels of the second parameter from this pair;

2) the plan-matrix of the experiment possesses the orthogonality property, i.e. each level of one input parameter meets only once with each level of any other input parameter.

The satisfaction of these two conditions makes it possible to obtain averaged partial dependences of the influence of any separate input parameter on a separate output parameter. In this case, the influence of all other parameters on this pair dependence is averaged. In this case, the influence of any input parameter on any output parameter can be represented graphically. With the number of input parameters that is more than two, the experiment plan based on Latin (for three input parameters) or Greek-Latin (for the number of input parameters more than three) squares meets these requirements. In this case, the number of levels of a change of each parameter should be the same for all input parameters and odd (the exception is the experiment plan for five input parameters at four levels [15]) and the number of input parameters should not exceed the number of levels by more than one. With the number of input parameters that is more than two, the experiment plan based on Latin (for three input parameters) or Greek-Latin (for the number of input parameters of more than three) squares meets these requirements. If the number of input parameters is equal to two, any restrictions on the number of levels of either of

the two parameters are removed. With the number of input parameters that is equal to two, the plan-matrix is a full-factor experiment with the number of experiments equal to the product of the number of levels of a change in the value of the first input parameter by the number of levels of a change in the value of the second input parameter.

The PDP method implies the construction of a multifactorial mathematical model of the process under study. To do this, first of all, a mathematical description of the graphs of particular dependences is given using one of the suitable methods of approximation (the least-squares method, the graphic-analytical method, the visual-analytical method [16], etc.).

Subsequently, to construct a multifactorial statistical mathematical model (generalized equation), the formula proposed by M. Protodyakonov [17] is used:

Fig. 1. Chemical structures of compounds used

$$Y_o = \frac{\prod_{i=1}^n Y_i}{Y_{cp}^{n-1}}, \tag{1}$$

where Y_o is the generalized equation; Y_i is a particular function; $\prod_{i=1}^n Y_i$ is the product of all particular functions; n is the number of particular functions that is equal to the number of input parameters; Y_{cp}^{n-1} is the general mean of all considered values of the generalized function in the degree that is less by unity than the numbers of particular functions.

The resulting generalized equation is usually used to optimize the process. The reliability of the obtained mathematical model is determined by calculating the coefficient of nonlinear multiple correlation [18]:

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

where n is the number of experiments; p is the number of input (independent) parameters; i is the number of an experiment by order; y_i is the actual magnitude of an input parameter in the i -th experiment; \hat{y}_i is the estimated magnitude of the input parameter calculated using the multi-factor mathematical model for the conditions (values of input parameters) of the i -th experiment; \bar{y} is the mean value of the actual magnitude of an input parameter for all n experiments (general mean).

In total, 6 systems that differed in the nature of the SAS and the nature of film-forming substance were explored. The wetting of the titanium dioxide substrate with each of these systems was studied. For the system “Uralkyd – white spirit – SAS – titanium dioxide”, the influence of the concentration of the SAS solvent on edge wetting angle (%) was explored. The SAS content (g/dm³) varied at three levels (0, 2, and 4). The solvent content (%), varied at three levels (30, 50, and 70).

The boundary values of the concentrations of additives and solvent content were selected based on the technological objectives in a particular paint and varnish material. Thus, the total number of experiments for each system was 3*3=9. Table 1 shows the factors under consideration and their respective levels.

Table 1

Table of experiments for each SAS for the system “Uralkyd – white spirit – SAS – titanium dioxide”

No. of experiment	Content of SAS, g/dm ³	Content of solvent, %
1	0	30
2	0	50
3	0	70
4	2	30
5	2	50
6	2	70
7	4	30
8	4	50
9	4	70

For the system “pentaphthalic resin – white spirit – SAS – titanium dioxide”, the influence of the concentration of the solvent of SAS (%) on edge wetting angle was studied. The surfactant content (g/dm³), varied at three levels (0, 16,

and 32). The solvent content (%), varied at three levels (30, 50, and 70).

The boundary values of the concentrations of the additives and the content of the solvent were selected based on the technological aims in a particular paint and varnish material. Thus, the total number of experiments for each system was 3*3=9. Table 2 shows the factors under consideration and their respective levels.

Table 2

Table of experiments for each SAS for the system “pentaphthalic resin – white spirit – SAS – titanium dioxide”

No. of experiment	Content of SAS, g/dm ³	Content of solvent, %
1	0	30
2	0	50
3	0	70
4	16	30
5	16	50
6	16	70
7	32	30
8	32	50
9	32	70

In the study, the effect of surfactants on the wettability of the pigment was estimated by the value of the angle between the solid surface and the tangent at the point of contact of the three phases, the so-called edge wetting angle θ in Fig. 2.

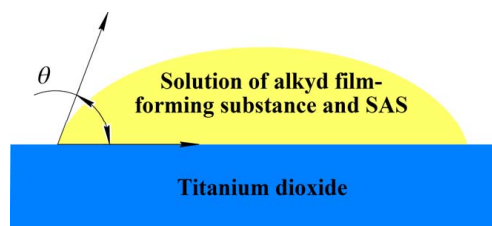


Fig. 2. Scheme for determining edge wetting angle θ°

Titanium dioxide of the R-02 brand (GOST 9804-84) of rutile form (mass fraction of titanium dioxide of rutile form is 95 %) made in the form of a round plate (diameter 80 mm, thickness 10 mm) was used as a substrate. During the research, edge wetting angles were determined at the boundary “solution of film-forming substance – titanium dioxide – air” (θ°) at a constant temperature (25 ± 0.5) °C.

The method for preparation of solutions was as follows:

- 1) the film-forming substance was poured into a sealed reactor (volume (0.2±0.01) dm³, filling factor – 0.60);
- 2) the solvent was added to the film-forming substance (ranged from 30 to 70 %);
- 3) the SAS that was previously dissolved in white spirit was introduced in specified quantities;
- 4) the reactor lid was hermetically closed and a stirring device (impeller stirrer, speed of 300 min⁻¹) was started;
- 5) after 30 minutes of stirring, the stirrer was disconnected and the lid was opened;
- 6) next, the samples of solutions, by using a pipette (the volume of a drop of 20 microliters), were placed on a substrate made of titanium dioxide, and the edge wetting angle was measured.

Edge wetting angle was determined by the results of the analysis of five parallel samples.

Adhesion of the film-forming solution to the surface of the solid substrate (in our case titanium dioxide) is characterized by work necessary to break the unit of the area of the interphase surface layer – work of adhesion W_a (J/m^2). Adhesion work was found from the combined Dupré-Young equation:

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

where δ_{l-g} is the surface tension at the boundary of “film-forming solution – air”, J/m^2 ; θ is the edge wetting angle of titanium dioxide (degrees).

5. Results of studying the pigment wettability

5.1. Studying the edge angle of wetting the pigment in alkyd paint and varnish materials

The introduction of additives into a pure solvent (white spirit) causes a decrease in the edge wetting angle (θ°) of titanium dioxide, Fig. 3, *a*. The introduction of SAS in uralkyd solutions causes a decrease in the edge wetting angle (θ°) of titanium dioxide, Fig. 3, *b–d*.

As the solvent content in the compositions increases, edge wetting angles θ° increase, Fig. 4.

Edge wetting angle was determined by the results of the analysis of five parallel samples, then the mean value, which was later used to process the results of experiments, was calculated.

Introduction of SAS into solutions of pentaphthalic film-forming substance causes a decrease in edge wetting angle (θ°) of titanium dioxide, Fig. 5.

The influence of the solvent content on edge angles of wetting of titanium dioxide with solutions of pentaphthalic film-forming substance is shown in Fig. 6.

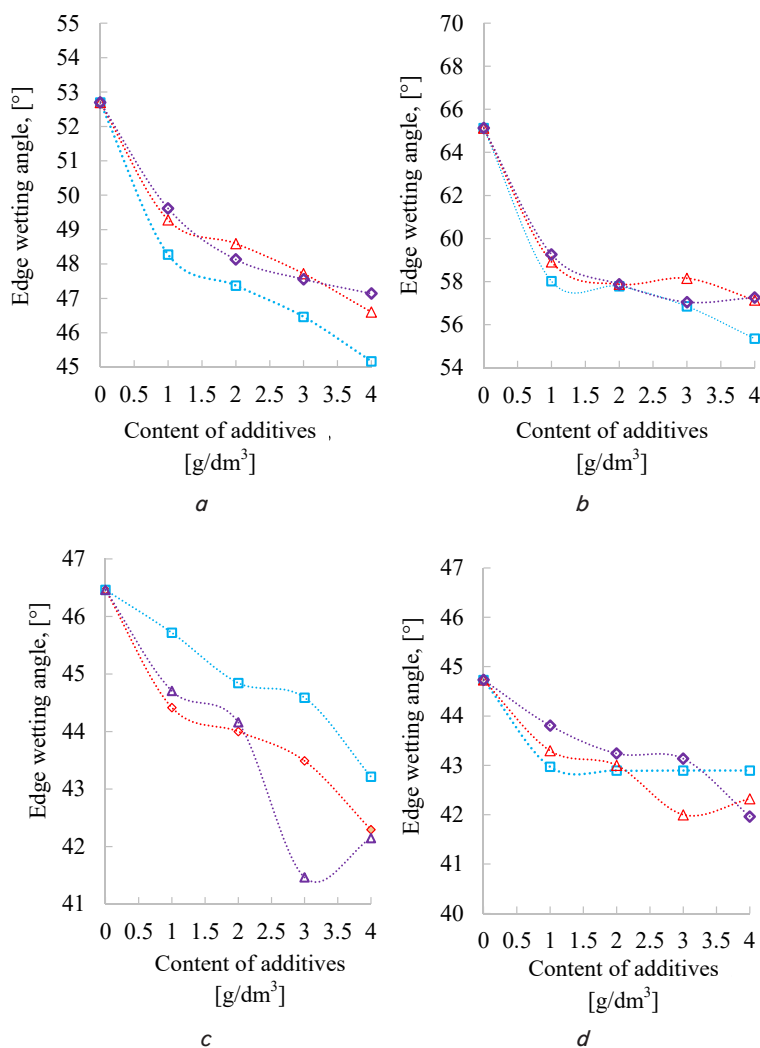


Fig. 3. Influence of the type and content of additives on edge angle of wetting titanium dioxide with solutions of uralkyd in white spirit: *a* – in a pure solvent; *b* – 90 % solvent; *c* – 70 % solvent; *d* – 50 % solvent; \square – Telaz; \triangle – PEPE; \diamond – AS-1

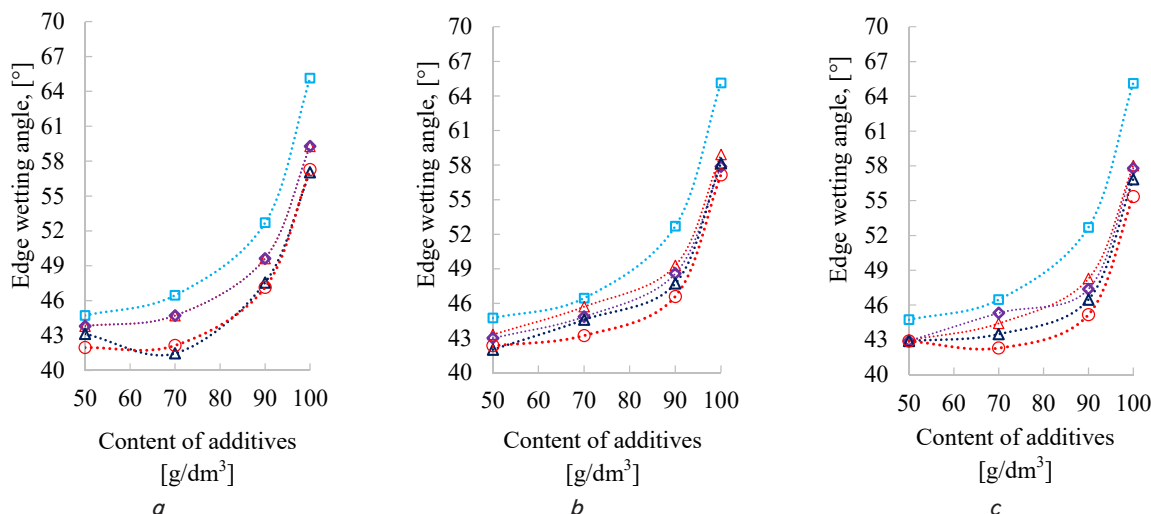


Fig. 4. Influence of the solvent, type and content of additives on edge angle of wetting of titanium dioxide with solutions of uralkyd in white spirit: *a* – AS-1; *b* – Telaz; *c* – PEPA; \square – without additives; \triangle – 1 gram/dm³; \diamond – 2 gram/dm³; ∇ – 3 gram/dm³; \circ – 4 gram/dm³

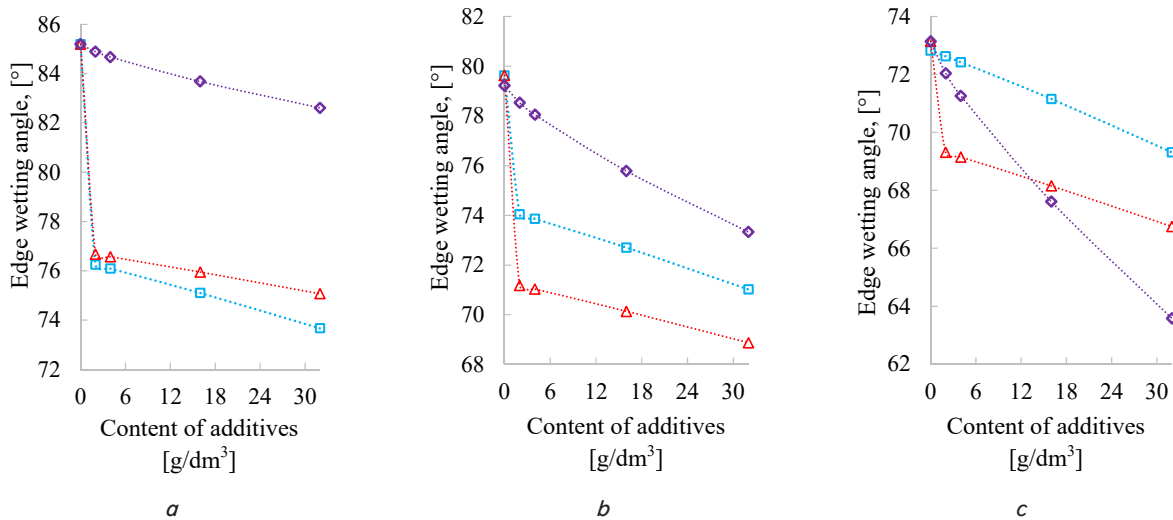


Fig. 5. Influence of the type and content of additives on edge angle of wetting of titanium dioxide with solutions of pentaphthalic resin in white spirit, at the content of *a* – 10 % solvent; *b* – 30 % solvent; *c* – 50 % solvent;
 ●—■— — Telaz; ●—▲— — PEPA; ●—◆— — AS-1

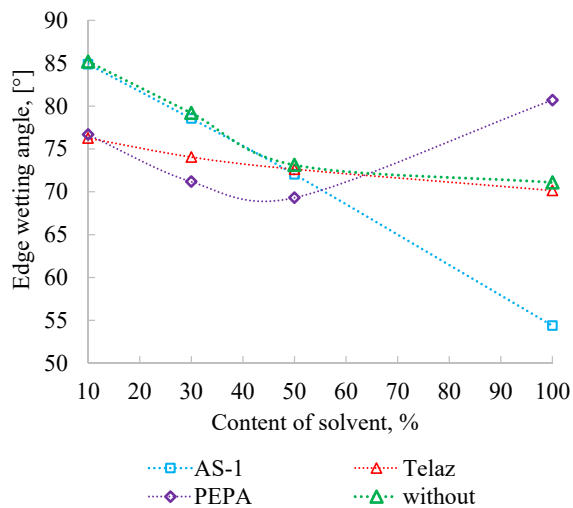


Fig. 6. Influence of the solvent and the type of surfactant on edge angle of wetting titanium dioxide with solutions of pentaphthalic resin in white spirit (at the content of the additive of 2 g/dm³)

The influence of the content of solvent on edge angles of wetting of titanium dioxide is not unambiguous. For most additives, an increase in the solvent content decreases the edge wetting angle. However, this effect is not found for the PEPA.

5. 2. Studying the adhesion work of solutions of pentaphthalic and alkyd-urethane film-forming substances on titanium dioxide

The introduction of additives in a pure solvent (white spirit) causes an increase in adhesion of white spirit of solutions on titanium dioxide, Fig. 7, *a*.

The introduction of SAS in the composition of uralkyds ambiguously affects adhesion work, Fig. 7, *b, c*. The introduction of additives in solutions of pentaphthalic film-forming substance causes a decrease in adhesion work on titanium dioxide, Fig. 8.

For AS-1, in the presence of pentaphthalic film-forming substance as the content of additive in the composition increases, adhesion work decreases equally. Under similar conditions, for PEPA and Telaz, adhesion work does not decrease linearly (there are inflection points).

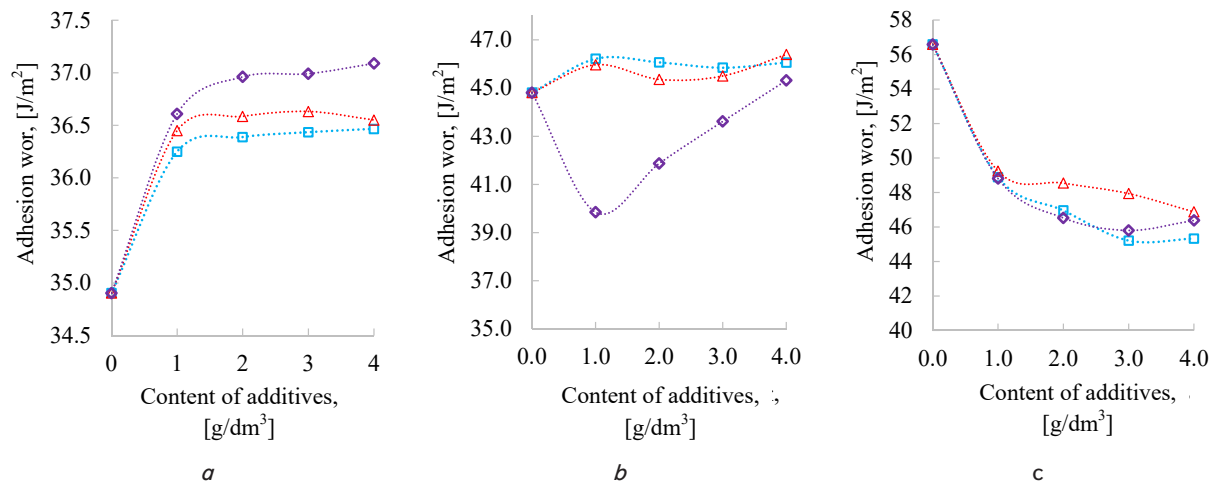


Fig. 7. Influence of the kind and content of surfactant on adhesion work W_a [J/m²] of solutions of uralkyd in the white spirit in titanium dioxide: *a* – 100 % solvent; *b* – 90 % solvent; *c* – 50 % solvent;
 ●—■— — Telaz; ●—▲— — PEPA; ●—◆— — AS-1

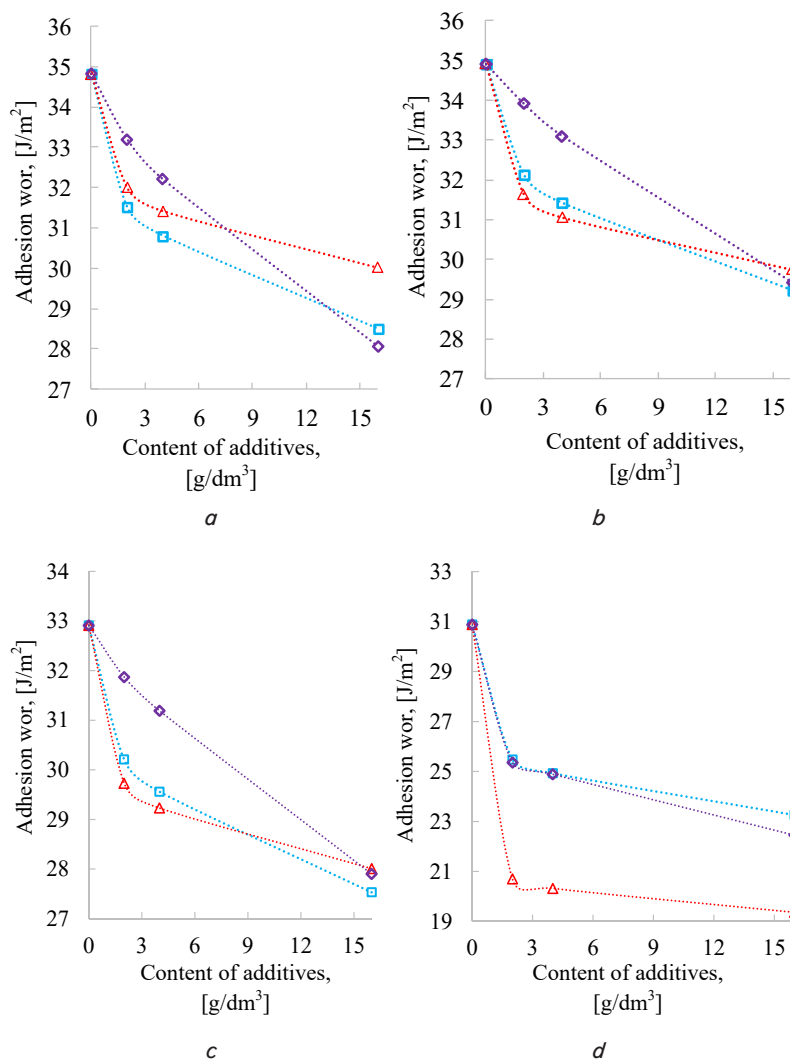


Fig. 8. Influence of the type and content of surfactants on adhesion work W_a [J/m²] of solutions of pentaphthalic film-forming in white spirit on titanium dioxide at the content: *a* – 10 % solvent; *b* – 30 % solvent; *c* – 50 % solvent; *d* – 100 % solvent; \square – Telaz; \triangle – PEPA; \diamond – AS-1

5.3. Optimization of compositions of paint and varnish materials, ensuring maximum wetting of the pigment

To derive a multifactorial statistical mathematical model of the influence of surfactants and solvent content on the wettability of titanium dioxide, the formula (1) was used. As a result, the influence of the concentration of the SAS and the solvent on wetting of titanium dioxide for each of the systems is described by the equation:

$$\theta = \frac{(a_1 + a_2 \cdot C_{surf.} + a_3 \cdot C_{surf.}^2) \cdot (b_1 + b_2 \cdot C_{solv.} + b_3 \cdot C_{solv.}^2)}{\bar{\theta}} \quad (4)$$

where θ is the edge wetting angle, °; $C_{solv.}$ is the content of the solvent, %; $C_{surf.}$ is the concentration of the SAS in solution, g/dm³; $a_1, a_2,$ and a_3 are the coefficients, characterizing the influence of the SAS on edge wetting angle, Tables 3, 4; b_1, b_2 and b_3 are the coefficients characterizing the edge wetting level, Tables 3, 4; $\bar{\theta}$ is the coefficient characterizing the influence of the substrate surface on the edge wetting angle.

Table 3

Value of coefficients for equation 2 for the system “Pentaphthalic film-forming substance – SAS – solvent”

SAS	Influence of concentration of SAS			Influence of concentration of solvent			$\bar{\theta}, \text{ }^\circ$
	a_1	a_2	a_3	b_1	b_2	b_3	
AS	74.5	-2.2	0.3	89.0	-0.3	0.0004	72.3
Telaz	74.6	-1.3	0.2	84.0	-0.3	0.0022	73.2
PEPA	74.7	-1.8	0.2	90.3	-0.7	0.0075	72.5

Table 4

Value of coefficients for equation 2 for the system “Uralkyd – SAS – solvent”

SAS	Influence of concentration of SAS			Influence of concentration of solvent			$\bar{\theta}, \text{ }^\circ$
	a_1	a_2	a_3	b_1	b_2	b_3	
AS	44.8	1.00	-0.42	43.2	0.01	-0.00002	43.9
Telaz	44.8	-0.73	-0.01	41.4	0.02	0.0004	43.2
PEPA	44.8	-0.84	0.06	41.1	0.01	0.0005	43.5

The reliability of the obtained mathematical model was estimated by calculating the coefficient of nonlinear multiple correlation (2). The minimum coefficient of nonlinear multiple correlation of the proposed mathematical model is 0.85.

5. 4. Effectiveness of the product AS-1 as a wetting additive for alkyd paints and varnishes

The original product AS-1 significantly decreases the edge angle of wetting of titanium dioxide in white spirit, as at its content in the composition of 4 g/dm³, the decrease in θ° is 8°. Under similar conditions, $\Delta\theta^\circ$ for Telaz is 10° (from 65° to 55°), and for PEPA 8° (up to 57°). Therefore, the wetting activity of AS-1 in pure white spirit is close to the industrial additive PEPA.

In solutions of Uralkyd and pentaphthalic film-forming substances, AS-1 shows significant wetting ability. Moreover, its maximum wetting activity is characteristic of high concentrations of SAS, over 2 g/dm³. For uralkyd film-forming substance (the 30 % content in the system), at a content of AS-1 of 4 g/dm³, $\Delta\theta^\circ$ is 4.5°, for a pentaphthalic composition, it is 10°.

6. Discussion of results of studying the pigment wetting

Additives for depression θ° in a pure solvent (white spirit) can be arranged in a row (as the wetting ability decreases): Telaz>PEPA>AS-1. However, in general, the values of depression of edge wetting angles for all the studied SAS are very close.

The introduction of SAS in uralkyd solutions causes a decrease in the edge wetting angle (θ°) of titanium dioxide, Fig. 3, *b–d*. However, in solutions with uralkyd resin, in contrast to the pure solvent, different SAS in various concentration ranges, rather than a specific additive have a higher wetting ability. At the 70 % content of a solvent in the composition, Fig. 3, and at concentrations of the SAS up to 2 g/dm³, Telaz is most effective. At the content of additives of above 2 g/dm³, the most effective wetting agent is AS-1, $\Delta\theta^\circ$ is 4.5° for it (from 46.46° to 41.96°), under similar conditions for PEPA and Telaz $\Delta\theta=4^\circ$. Another difference of the SAS solutions with uralkyd resin from solutions in a pure solvent is a more equal increase in wettability of the substrate (i.e., the absence of sharp inflections on the graph $\theta=f(C_{surf})$ characteristic of SAS solutions in a pure solvent), Fig. 3, *b–d*. As the solvent content in the compositions increases, regardless of the type used by the SAS, edge wetting angles θ° increase. Additives for depression θ° in solutions of pentaphthalic film-forming substance can be arranged in a row (as wetting ability decreases):

- in solutions with a solvent content of 10%: Telaz>>PEPA>AS-1;
- in solutions with a solvent content of 30%: PEPA>Telaz>AS-1;
- in solutions with a solvent content of 50%:
- at the content of SAS up to 18 g/dm³: PEPA>>AS-1>Telaz;
- at the content of SAS from 18 to 32 g/dm³: AS-1>PEPA>Telaz.

In the absence of surfactants in solutions of pentaphthalic film-forming substance, as the solvent content increase, we observe a decrease in edge wetting angle. Consequently, the film-forming substance itself demonstrates in the solution the properties of surfactants, which is consistent with

the data in the literature. In the presence of high-molecular additives PEPA and Telaz, the character of dependences $\theta=f(C_{surf})$ is generally close to dependence

$$\theta=f(C_{\text{PENTAPHTHALIC FILM-FORMING SUBSTANCE}}).$$

However, for the most low-molecular SAS – AS-1, the nature of dependences $\theta=f(C_{surf})$ has a completely different “linear” character. As the solvent content increases, wetting of the substrate with AS-1 solutions invariably increases.

The introduction of additives into a pure solvent (white spirit) causes an increase in adhesion work of white spirit solutions on titanium dioxide, Fig. 7, *a*. The most effective additive in a pure solvent is AS-1; W_a increases by 2 J/m² (from 34.9 to 37.09 J/m² at the content of the additive of 4 g/dm³). For other additives under similar conditions, the change in wetting work is not more than 1.5 J/m².

The introduction of SAS to the composition of uralkyds, in contrast to solutions of additives in a pure solvent, ambiguously affects adhesion work, Fig. 7, *b, c*.

At low contents of uralkyds in compositions (10 %, Fig. 7, *b*), adhesion work for PEPA and Telaz increases to the SAS concentration of 1 g/dm³ and then gets stabilized at the level of 45.5...46,2 J/m². However, AS-1 under similar conditions behaves completely differently: first, in the range of up to 1 g/dm³ W_a decreases by 5 J/m². And then, at an increase in the content of AS-1 of above 1 g/dm³ W_a equally increases to 45.31 J/m².

For solutions of pentaphthalic film-forming substance, AS-1 is the most effective additive, minimally reducing adhesion work, Fig. 8. In the presence of high-molecular additives PEPA, Telaz, and pentaphthalic film-forming substance, Fig. 8, *a–c*, the character of dependences $W_a=f(C_{surf})$ are generally close. However, for the most low-molecular SAS – AS-1, the character of dependences $W_a=f(C_{surf})$ has a slightly different, more “linear” character. As the content of AS-1 increases, W_a invariably decreases. In a pure solvent (without a pentaphthalic film-forming substance), the character of dependences $W_a=f(C_{surf})$ for all three SAS is identical. In general, we can conclude that the introduction of additives into alkyd PVM causes a decrease in adhesion work. This is not a positive point, but it emphasizes the superficial activity of the studied film-forming substances.

The obtained results can be explained by the possible adsorption of the studied additives at the active/adsorption centers of titanium dioxide. As a result, the hydrophobicity of the pigment surface increases, and the wetting of titanium dioxide increases.

The features of the obtained results are that this study compares three different nitrogen-containing additives (two of them are industrial additives, and one is original SAS), having different molecular weights. For a complete understanding of the mechanism of influence of the considered surfactants on wetting of titanium dioxide with solutions of alkyd film-forming substances, it is necessary to study their adsorption on the pigment and influence of additives on viscosity and other parameters of solutions.

Using the PDP method and based on equation (4), the optimal contents of the SAS and solvent in enamels, ensuring maximum wetting of the pigment, were determined.

For the resulting additive AS-1, the nomograms were constructed to find θ° according to the known contents of the SAS and the solvent, presented in Fig. 9.

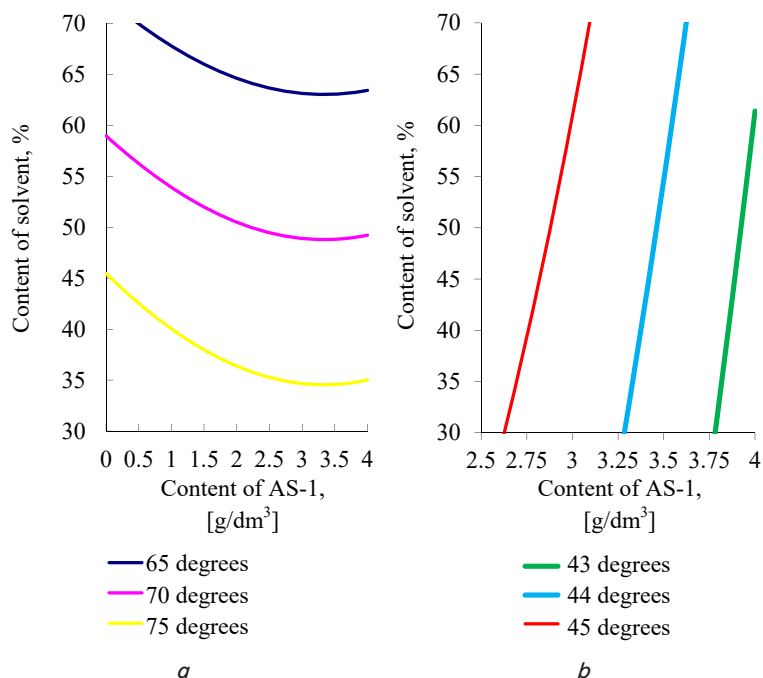


Fig. 9. Nomograms $\theta^\circ = f(C_{AC-1}, C_{solvent})$: *a* – for pentaphthalic foam-forming substance; *b* – for alkyd-urethane film-forming substance

This study was conducted under isothermal conditions (at a temperature of 25 °C), so it does not take into consideration the temperature fluctuation in the process of obtaining and transporting paints and varnishes and formation of a paint and varnish coating. When the temperature changes, fluctuations in the surface tension of film-forming solutions at the interphase boundaries “solution of PVM – air” and edge wetting angle can significantly change adhesion work.

A logical continuation of this study is the study of the influence of the considered additives on the protective, physical, mechanical, and decorative properties of coatings. In addition, it would be interesting to test the influence of the studied additives on the dispersion and aggregative resistance of suspensions.

The proposed product AS-1 can be successfully used as a wetting additive for uralkyd and pentaphthalic paint and varnish materials. The wetting ability of AS-1 in the studied paint and varnish materials is close to the industrial additives-dispersers PEPA and Telaz. These additives are produced in hundreds/tens of tons annually and are common additives for the paint and varnish industry. However, the original product AS-1 is synthesized from oil refining waste, which is one of the ways to reduce the burden on the environment (less emission of substances will fall into nature).

7. Conclusions

1. All the studied additives in the alkyd-urethane and pentaphthalic compositions improve the wetting of titanium

dioxide. At the 30 % content of the alkyd-urethane film-forming substance in the composition, the maximum reduction of θ° for AS-1 is 4.5°, for PEPA and Telaz – 4°. For the pentaphthalic composition under similar conditions, the reduction of the edge wetting angle for AS-1 is 10°, for Telaz 8.6°, and for PEPA 5.9°. SAS better show wetting activity in the pentaphthalic composition, judging by a decrease in θ° (10° instead of 4.5° for uralkyds), but by the relative change in edge wetting angle for both systems $\Delta\theta^\circ$ is about 10 %. The wetting activity of the original product AS-1 is close to industrially produced additives used in paints and varnishes.

2. The introduction of SAS into the composition of alkyd-urethane film-forming substance ambiguously influences adhesion work (W_a). For pentaphthalic compositions, the introduction of additives causes a decrease in adhesion work (W_a) on titanium dioxide. At a 30 % content of pentaphthalic film-forming substance in the composition, the maximum decrease in W_a for AS-1 is 5.5 J/m², for PEPA 5.2 J/m² and for Telaz 5.68 J/m².

3. With the help of probabilistic-deterministic planning, an equation for calculating $\theta^\circ = f(C_{surf}, C_{solvent})$ was derived. Optimization of the compositions of alkyd-urethane and pentaphthalic paint and varnish materials, which ensures maximum wetting of titanium dioxide with film-forming solutions, was performed. In industrial pentaphthalic enamel, the maximum edge wetting angle of 75° is achieved with a 40 % solvent content and content of AS-1 of 1 g/dm³. In alkyd-urethane enamel, the maximum edge wetting angle of 44° is achieved with a 40 % solvent content and the content of AS-1 of 2.75 g/dm³.

4. The effectiveness of the product AS-1 as a wetting additive for alkyd-urethane and pentaphthalic paint and varnish materials was proven. The wetting ability of AS-1 in the studied pentaphthalic and uralkyd enamels is close to the industrial additives-dispersers PEPA and Telaz. However, the original product AS-1 is synthesized from oil refining waste, which is one of the ways to reduce the burden on the environment (less emission of substances will fall into nature).

Since the initial substance for the synthesis of AS-1 is a waste product of oil refining, the cost of this product will be low. And in the context of a recession of the world economy, the need for cheap additives for the paint and varnish industry will only increase. According to TU 655-RK 05606434-001-2000, the original product AS-1 is recognized as a substance with minimal harmfulness, class IV, according to GOST 12.1.007-76.

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