UDC 661.1:541.18
DOI: 10.15587/1729-4061.2021.239208

DEVELOPMENT OF SEDIMENTATION RESISTANT WATER-ACRYLIC TITANIUM DIOXIDE DISPERSIONS

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According to the results of the research, the effect of stabilization of dispersions of titanium dioxide in water-acrylic compositions was established. It was proved that in aqueous-acrylic suspensions at all variations of film-forming agent (from 0 to 5 g/dm^3), the maximum of stabilizing activity of the surfactants under study is achieved at CSAS=0.25 g/dm^3. The minimum deposition rate of titanium dioxide dispersions at a dosing of 0.25 g/dm^3 of sodium polyacrylate was at the level of 0.097 10^{-3} g/s at any content of film-forming agent (Cff=0.5÷5 g/dm^3) in suspensions. At the introduction of the same concentration (CSAS=0.25 g/dm^3) of the polyether siloxane copolymer, a decrease in sedimentation rate to 0.053 10^{-3} g/s in suspensions with a limited acryl content (C≤1 g/dm^3) was recorded. At an increase in the concentration of a film-forming agent (C>1 g/dm^3) in suspensions, sedimentation stability decreased, which is proved by an increase in the sedimentation rate of TiO_2 to 0.110·10^{-3} g/s at Cff=5.0 g/dm^3. It was found that in aqueous-acrylic suspensions with the film-forming content from 0.5 to 1 g/dm^3, the minimum average diameter was 2.64÷3.1 µm CSAS=0.25 g/dm^3. Further concentration of acryl (Cff=4÷5 g/dm^3) at the same dosage of polyether siloxane copolymer was accompanied by an increase in the average particle size up to 4.30÷4.61 µm. The maximum of wedging activity of sodium polyacrylate (CSAS=0.25 g/dm^3) corresponds to the same minimum of the average diameter (2–3 µm)

Keywords: water-acrylic compositions, adsorption, titanium dioxide, sodium polyacrylate, polyether siloxane copolymer

Received date 28.06.2021
Accepted date 10.08.2021
Published date 31.08.2021

***How to Cite**: Dyuryagina, A., Lutsenko, A. (2021). Development of sedimentation resistant water-acrylic titanium dioxide dispersions. Eastern-European Journal of Enterprise Technologies, 4 (6 (112)), 51–59. doi: https://doi.org/10.15587/1729-4061.2021.239208*

1. Introduction

The implementation of a uniform distribution of pigment particles can be achieved by ensuring the sedimentation stability of the system before polymerization begins. Conditions of uniform distribution of pigment are determined primarily by the colloidal-chemical properties of the system, namely dispersity and polydispersity of pigment particles, the state of its surface, sedimentation and aggregative stability. That is why the colloidal-chemical approach makes it possible to obtain polymeric materials with specified properties. One of the main methods for purposeful regulation of the properties of polymer composite materials and coatings is the use of surfactants (SAS). In the technology of polymeric paint and varnish materials and coatings, the use of amphiphilic polymer compounds of various chemical compositions is constantly expanding. As a result of adsorption phenomena, their physical (and sometimes chemical) interaction with the surface of dispersed particles and substrates, associations with film-forming molecules, the deformation-strength, insulating, adhesive, coloristic, and other properties of paint and varnish coatings can change significantly.

Despite a large number of papers devoted to the study of the effect of surfactants on the properties of composite polymeric materials, the influence of polymer surfactants on the distribution of solid-phase pigment particles in a paint composition, in particular, the one based on polyesters, has not yet been sufficiently studied. Their reasonable choice is necessary to obtain polymer coatings with a given set of properties. This determines the relevance of research.

2. Literature review and problem statement

In the process of preparing paint and varnish compositions, a more energetically advantageous (in comparison with air) interfacial surface appears at the time of combining a film-forming agent with the pigment in the dispersive medium [1]. The pigment becomes a kind of matrix for the formation of adsorption layers of all available surfactants. A change in the adsorption-solvate layers formed at the interfacial boundary "pigment – dispersion medium" at the introduction of surfactants (SAS) into the composition of paint and varnish compositions opens up the possibility of fine regulation of the processes of disaggregation and stabilization of pigment particles [2, 3]. The disaggregating effect of surfactants is based on the effect of an adsorptive decrease in the strength of pigment aggregates. Surfactants, diffusing from the volume of the dispersion medium, penetrate the internal cavities of aggregates, in which they generate positive wedging pressure (Rehbinder effect), which contributes to their separation. The separation of large pigment agglomerates into small ones causes an increase in the number of solid-phase particles and, as a result, free interfacial energy of the heterogeneous system. Meanwhile, as it is known [4], the free energy of the system always tends to decrease, so in dispersed systems, the processes accompanied by a decrease in this energy can always flow spontaneously. As a result, disaggregated pigment particles that do not have sufficient adsorption coating again form coagulation structures or floccules with a smaller reserve of surface energy, which makes the system aggregately unstable [5]. Aggregate instability, which reduces the final degree of dispersion, entails sedimentation (kinetic) instability associated with the gradual deposition of solid particles under the influence of gravity [6, 7]. The greater the difference of polarity between the dispersed phase and the dispersive medium, the stronger the tendency of the dispersed phase particles to aggregate [8, 9]. During sedimentation, large particles moving at a higher speed can catch up with slowly settling particles and "capture" them. The probability of such adhesion of large and small particles depends on the ratio of their settling rates, as well as on conditions of adhesion of small particles to the surface of larger ones. It was shown that when very large particles settle, particles close in size and very small ones are most effectively captured [10]. Intermediate-sized particles are captured worse. This is due to the fact that the smallest particles diffuse to the surface of a larger particle during its overflow by a liquid, and the diffusion will accelerate under the action of molecular forces of attraction. Particles with a size approaching the size of a large particle are mainly influenced by inertial forces that occur at the beginning of the overflow when the motion of a liquid is directed from the axis of settling of a large particle towards the side. The convergence of particles is due to the action of these inertial forces, and only at the smallest distances, the molecular forces become significant, which causes them to stick together. Particles of intermediate sizes are captured worse because both inertial forces and diffusion rate are relatively small for them [11].

To prevent the above processes, the stabilization of pigment dispersions, which is determined by the nature of molecular forces, particle surfaces, and electrical charges, is required. The mechanism of the interaction between the pigment-dispersion medium depends on these factors. The theory, which is based on ideas about the structural and mechanical factors of stability of dispersed systems and spatial grids such as coagulation structures, is most applicable to such interactions.

The basic principles of stabilization of pigment dispersions follow modern ideas about the stability of colloidal systems. For pigmented paints and varnishes, stabilization due to the structural and mechanical properties of the adsorption layers is of the greatest importance. Adsorption layers, especially in the case of the formation of spatial structures, make steric obstacles to the convergence of pigment particles to the distance of effective action of attractive forces between them and also reduce the reserve of surface energy, interaction with the active centers of the solid surface of the particles. In addition, when pigment particles come together and adsorption-solvate shells overlap, the so-called entropic repulsion plays its role. The theory of entropic repulsion as the main factor of stabilization puts forward the mandatory existence of vertically oriented SAS molecules in a firmly fixed adsorption layer [12]. Only long hydrocarbon chains with conformational mobility, vertically located towards a solid surface, cause entropic repulsion at mutual penetration. In this regard, diphilic compounds that play the role of surfactants of stabilizing action are of huge practical interest [13].

Diphilic low-molecular or oligomeric compounds [14], acrylic copolymers containing (meth)acrylic acid or their derivatives [13] are known to be used as additives of dispersing action. Polyether and siloxane copolymers, polyphosphates (mainly in matte latex paints), salts of oligocarboxylic acids, products of copolymerization of unsaturated simple polyethers (PEF), and unsaturated carboxylic acids or their anhydrides (maleic) are widely used [15].

The concept of surface activity of a substance is relative and is not its absolute property, it depends on the nature of the surface of the phase separation [16]. In this regard, it seemed expedient to study the stabilizing effect of two varieties of amphiphilic polymer compounds (polyether siloxane copolymer, sodium polyacrylate) in water-acrylic compositions with rutile titanium dioxide.

3. The aim and objectives of the study

The aim of the study is to determine the stabilizing effect of two different polymeric surfactants (polyether siloxane copolymer, sodium polyacrylate) in water-acrylic compositions with solid-phase particles of pigment (titanium dioxide). This will make it possible to evenly distribute pigment particles to obtain polymer coatings with a given set of properties.

To achieve the aim, the following tasks were set:

– to determine sedimentation rate of titanium dioxide dispersions in water-acrylic compositions in the presence of film-forming agent and surfactant;

– to reveal regularities of development of processes of disaggregation and sedimentation of dispersions depending on the content of acryl and introduced additives;

– to study the effectiveness of applying polyester siloxane copolymer (PES) and sodium polyacrylate (PAN) as stabilizing and dispersing surfactants;

– to assess the influence of concentration parameters of SAS and compositions on the dynamics of deposition of titanium dioxide particles.

4. Materials and methods of research

The influence of concentration modes of film-forming agent and surfactant on the sedimentation stability of titanium dioxide suspensions was determined by the weight method, the essence of which was the periodic weighing of the sediment collected on a cup of torsion scales (brand VT-500) [17].

In the experiments, the weight content of acrylic dispersion was varied by dilution with water ($Cff=0\div5$ g/dm$^{3),}$ the consumption of surfactants ($CSAS=0\div4$ g/dm^3). The weight of titanium dioxide in suspensions was assigned as a constant of 0.1 g. Studies were carried out in thermostatic mode at a temperature of 20 °C.

For more complete wetting of titanium dioxide powder and stabilization of all equilibrium characteristics, the suspension was stirred for 30 minutes.

25 ml of suspension were poured into a cylinder of 50 ml and thoroughly stirred. Immediately after the end of stirring, a cup of the torsion scales was lowered into the center of the measuring cylinder and the stopwatch was turned on. The mass indicator was set by the tension level at a value of 0.14 g and the time to reach the specified weight on the calyx of the scales, immersed in the suspension, was recorded. Sedimentation rate was calculated from equation (1):

$$v=\frac{m}{\tau}, \tag{1}$$

where ν is the sedimentation rate, g/s; m is the sediment weight, g; τ is the time, s.

Based on the obtained data, kinetic dependences of sedimentation rate were constructed.

To study the regularities of dispersion of titanium dioxide in water-dispersive compositions, the own method for computer micro-optic analysis, which included computer fixation of microstructures of modified suspensions and their mathematical processing, was developed [18, 19]. The computer micro-optic method for suspension analysis makes it possible to automatically establish the regularities of development of the processes of disaggregation (aggregation) of solid-phase pigments. As the resulting indicator of disaggregation (aggregation), the average size of solid-phase dispersions (d, µm), which were calculated according to equation (2), was used:

$$d = 331.996 \cdot X^{-0.9585} \cdot \sqrt{\frac{S_p}{N}}, \qquad (2)$$

where X is the increase in computer micro-optic setup;

S_p is the total area of particles established by the results of computer micro-optic scanning of suspensions, pixel;

N is the total number of particles in the image, established by the results of computer micro-optic scanning of suspensions, pcs;

331.996 is the coefficient of conversion to metric units, µm/pixel$^{1/2}$.

These characteristics of the dispersive composition of suspensions (S_p, N) were determined by the results of microanalysis of three parallel samples. The suspensions were prepared at a temperature of 20 °C in a sealed reactor (volume 0.2 g/dm^3, filling factor – 0.60), equipped with a stirring device (impeller stirrer, rotation rate 300 min^{-1}). The dispersing effect was established in aqueous suspensions with a 1 % solid phase content. In suspensions, the quantitative content of surfactants from 0 to 4 g/dm^3, of the film-forming agent from 0 to 5 g/dm^3 was varied. The pigment content was determined by the results of preliminary tests. It was revealed that at a given multiplicity of an increase in the computer micro-optic system ×350, the best effect in terms of reproducibility and accuracy of the results is ensured when its content in aqueous suspensions at the level of 1 %.

Samples of 0.02 ml were taken from the resulting suspension with a pneumatic dispenser, which, after exposure under static load, were subjected to microanalysis.

As the solvent evaporates, the processes of triaxial compression of films develop. This is accompanied by a change in the geometric parameters (in plane x, y, and in height z) of the films themselves, as well as the formation of deformation shear forces (F) in relation to other objects, in particular, on the slide and cover glass. The problem for this factor was solved by the search for modes (by specific load and duration) that minimize shear deformations. When optimizing the load (P, g/cm^2) and its uniformity along the perimeter of the cover glass, on the one hand, we proceeded from the provision of the $P>F$ condition. As shown by the results of experimental studies on various samples (by volume and composition), this condition at a volume of suspensions of 0.02 ml (the volume of a drop once dosed with a pneumatic dispenser) is met at a load mode of at least P=30 g/cm^2. On the other hand, given that films are formed over time (which is determined by the rate of solvent evaporation) according to the exponential law, the modes of exposure of samples (under load) over time were experimentally optimized. The duration, which ensures relative stabilization of the deformation characteristics of suspension films, was 5 minutes.

The development of the adsorption process was controlled by measuring the surface tension of the liquid phase at the boundary with the air according to the standard ring tear-off method [20]. The maximum ring tear-off force was measured using a tensiometer of the DST model.

The duration of the experiments in all cases was 30 minutes, which, according to preliminary studies, was sufficient to achieve equilibrium states. Upon completion of operations, the components of the suspension were quickly separated by centrifugation, at the same temperature modes, at which experimental studies were performed. The amount of adsorbed surfactants (G, g/g of pigment) was determined by previously obtained calibration curves $\sigma=f(C_{SAS})$ for the corresponding compositions of film-forming agents. The values of surface tension for surfactant concentration of SAS were determined 5 times. The number of adsorbed additives on the solid surface of titanium dioxide was determined by the difference in their equilibrium concentrations in the solution (the ring tear-off method) before and after adsorption, at the fixed weight of the pigment (m=0.4 g), and at the constant volume of the solution (V=0.25 dm^3).

The viscosity of the tested solutions was determined using a capillary viscometer (d=0.86 mm). The principle of operation is based on calculating the time of flow of a given liquid volume through a narrow hole or a tube, at a given difference of pressures [21].

For each of the parameters, the standard deviation of the single determining of the measurement method was determined from formula (3):

$$S = \sqrt{\frac{\sum_{j=1}^{j=m} \sum_{i=1}^{i=n} \left(x_{ji} - \bar{X}_j\right)^2}{n-m}}, \qquad (3)$$

where m is the number of a sample; n is the total number of measurements; j is the sample number; $\bar{X}$ is the arithmetic mean of repeated observations for the conditions of this experiment.

For the method of determining the sedimentation rate, the total standard deviation S_v=0.0344·10^{-3} g/s, for the method of determining the average diameter S_d=0.6779 µm, for the method for determining adsorption S_A=7.9310^{-4} g/g.

In experiments, a standard deviation of single determining and confidence interval were determined for each surfactant system.

5. Results of the study of sedimentation and dispersing effects of SAS

5. 1. Rate of sedimentation of titanium dioxide dispersions in water-acrylic compositions in the presence of film-forming agents and additives

At the first stage, the influence of SAS on the rate of deposition of TiO$_2$ particles in water was studied, which excludes the possible influence of film-forming agents on sedimentation processes. The effect of two varieties of amphiphilic compounds in the solvent on sedimentation rate is characterized by the dependences shown in Fig. 1.

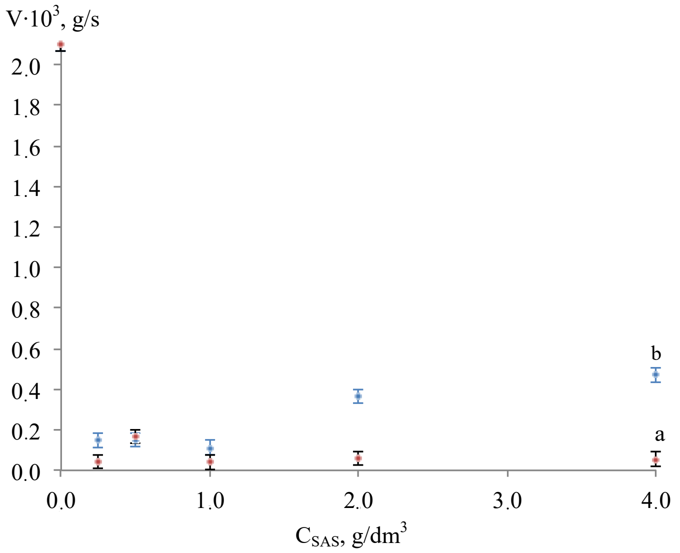


Fig. 1. Influence of surfactant concentration on the rate of pigment sedimentation in aqueous suspensions: *a* – sodium polyacrylate; *b* – polyether siloxane copolymer

The introduction of the SAS into the water was accompanied by significant changes in the kinetics of deposition of pigment particles. Judging by the nature of a change in the rate, the maximum stabilizing activity of both additives is observed when their content in the suspension is at the level of 1.0 g/dm^3. PAN (Fig. 1, curve *a*) has the greatest stabilizing effect; at an increase in its content in suspensions from 0 to 1.0 g/dm^3, sedimentation rate decreased by 53.2 times (relative to water without surfactants) and amounted to $0.039 \cdot 10^{-3}$ g/s. When changing within the quantitative contents of PES (Fig. 1, curve *b*) within the same limits, the value of V decreased to $0.112 \cdot 10^{-3}$ g/s.

Outside the specified concentration section (C_{SAS}>1 g/dm^3) in aqueous suspensions of titanium dioxide, a slight increase in the rate of sedimentation of pigment particles (V=$0.054 \div 0.061 \cdot 10^{-3}$ g/s) was recorded, while with PES this increase was more pronounced. The sedimentation rate in aqueous suspensions at a concentration of PES of 2 and 4 g/dm^3 was $0.364 \cdot 10^{-3}$ g/s and $0.469 \cdot 10^{-3}$ g/s, respectively.

5. 2. The dependence of processes of disaggregation and sedimentation of dispersions on the content of acryl and introduced additives

The nature of a change in the stabilizing activity of additives is explained within the framework of the established regularity of the development of processes of disaggregation of solid-phase pigment particles when they are combined with the aqueous dispersive medium of the studied suspensions (Fig. 2).

The introduction of both PAN (Fig. 2, curve *a*) and PES (Fig. 2, curve *b*) leads to the intensification of the processes of disaggregation of solid-phase particles of titanium dioxide as a result of adsorption decrease in the strength of pigment aggregates.

At the same time, one can trace a close correlation between these three dependences: the minimum sedimentation rate V (Fig. 1) corresponds to the minimum values of the average diameter d_{av} (Fig. 2) and the maximum spilling activity of the surfactant (Fig. 3).

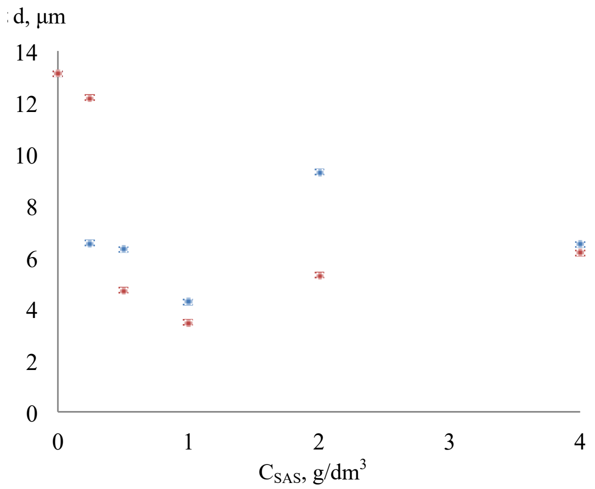


Fig. 2. Change in the average diameter of pigment particles in aqueous suspensions in the presence of surfactants: *a* – sodium polyacrylate; *b* – polyether siloxane copolymer

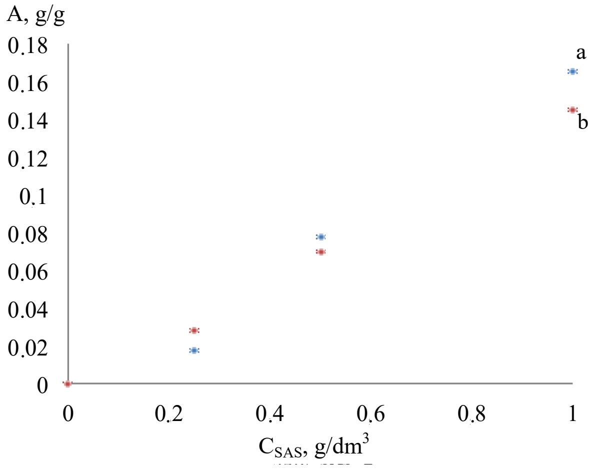


Fig. 3. Isotherms (T=298 K) of adsorption of additives on the surface of titanium dioxide: *a* – sodium polyacrylate; *b* – polyether siloxane copolymer

The maximum disaggregating effect in relation to titanium dioxide, judging by the nature of the change in average diameter (Fig. 2, curves *a* and *b*), was recorded in the same region of additive concentrations (C_{SAS}=1 g/dm^3). The average diameter decreased by 8.86 μm (PES) and by 9.65 μm (PAN) compared to unmodified aqueous suspension (d=13.12 μm).

5. 3. Effectiveness of polyether siloxane copolymer and sodium polyacrylate as stabilizing and dispersing additives

PAN, which ensures a greater decrease in interfacial surface energy at the boundary of separation of pigment and water (G=0.195 g/g at C_{SAS}=1 g/dm^3) than PES (G=0.145 g/g at C_{SAS}=1 g/dm^3), shows a greater increase in dispersing of titanium dioxide. As a result, with a slight change in viscosity of the dispersion medium (Table 1), in aqueous suspensions with PAN, smaller pigment particles settle more slowly than in suspensions with PES.

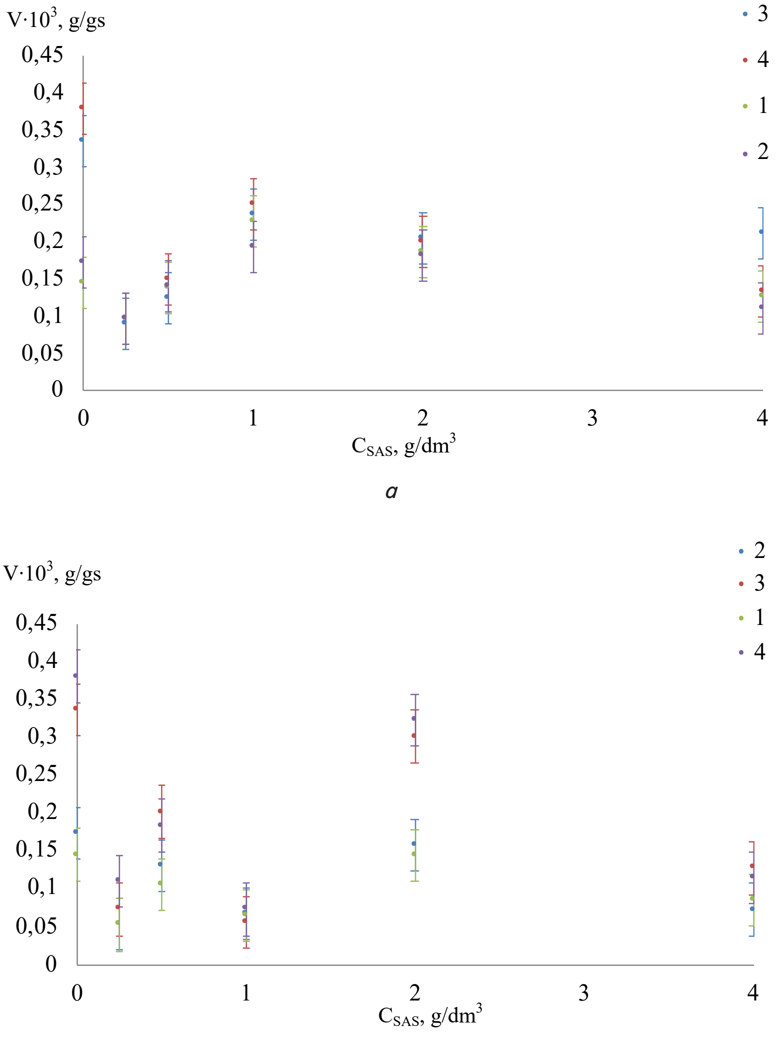
Table 1

Dependence of viscosity of dispersive medium of aqueous suspensions on the concentration of additives

η, Pa·s	C_{SAS}, g/dm^3					
	0	0.25	0.5	1	2	4
PAN	1.375	1.390	1.395	1.420	2.095	2.481
PES	1.375	1.380	1.395	1.410	1.901	2.225

At the second stage, studies on the influence of surfactants on the sedimentation rate of TiO_2 particles with different content of a film-forming agent in water were conducted. The influence of the nature and quantitative contents of additives on sedimentation stability of dispersions of titanium dioxide in water-acrylic suspensions reflects the dependences in Fig. 4.

Judging by a decrease in sedimentation rate at the introduction of 0.5 g/dm^3 of acryl into water (Fig. 4), part of the surface of titanium dioxide was blocked by film-forming macromolecules. This is evidenced by an increase in G values up to 0.05 g/dm^3 (Fig. 5).



a

b

Fig. 4. The influence of the content of a film-forming agent and concentration of SAS on sedimentation rate, *Cff*: 1 – 0.5 g/dm^3, 2 – 1 g/dm^3, 3 – 4 g/dm^3, 4 – 5 g/dm^3: *a* — sodium polyacrylate; *b* — polyether siloxane copolymer

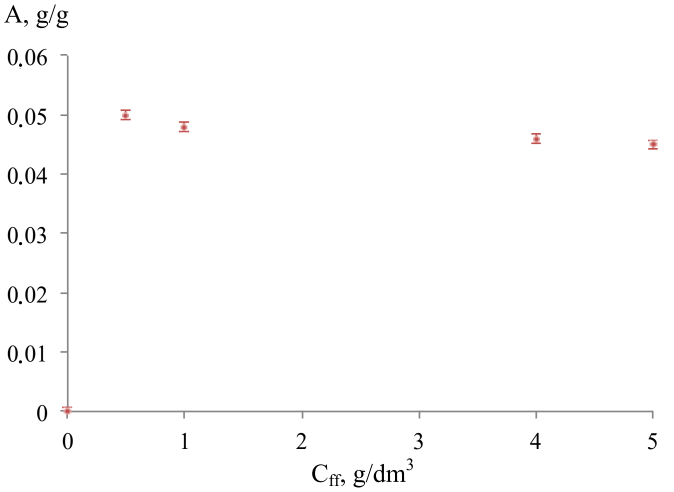


Fig. 5. Isotherm (T=298 K) of adsorption of film-forming agent of the pigment surface

A sharp decrease was observed, in the sense that in the absence of the SAS the sedimentation rate was 0.38·10^3 g/s, while at the addition of a modifier it decreased to 0.12·10^3 g/s.

Analysis of the obtained results shows that in the absence of surfactants (C_{SAS}=0 g/dm^3), sedimentation rate in suspensions depends on the content of film-forming agent in them. In comparison with the indicator of sedimentation of TiO_2 in water, the sedimentation rate of solid-phase particles decreases in the water-acrylic suspension (*Cff*=0.5 g/dm^3) by 15 times and is 0.145·10^3 g/s.

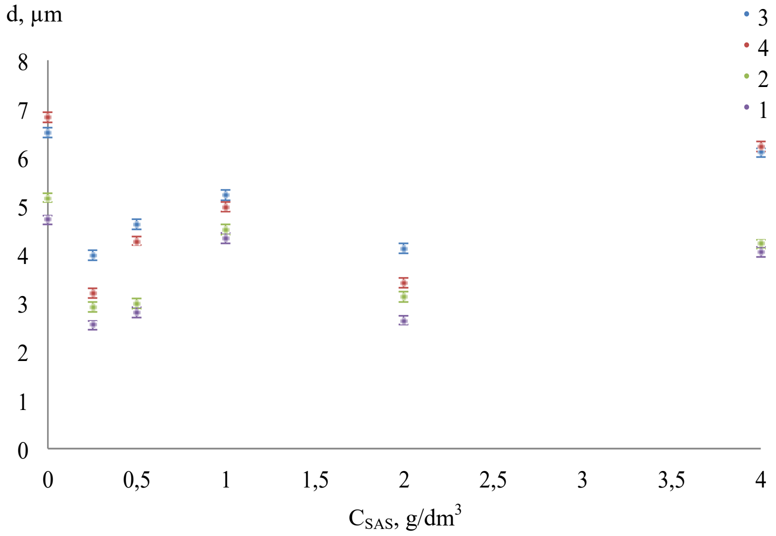
5. 4. Influence of concentration parameters of additives and composition formulations on the dynamics of sedimentation of titanium dioxide particles

It was found that the introduction of 0.5 g/dm^3 of acryl into water (Fig. 6) is accompanied by a decrease in the average diameter of pigment particles by 8.41 μm (from 13.12 to 4.71 μm).

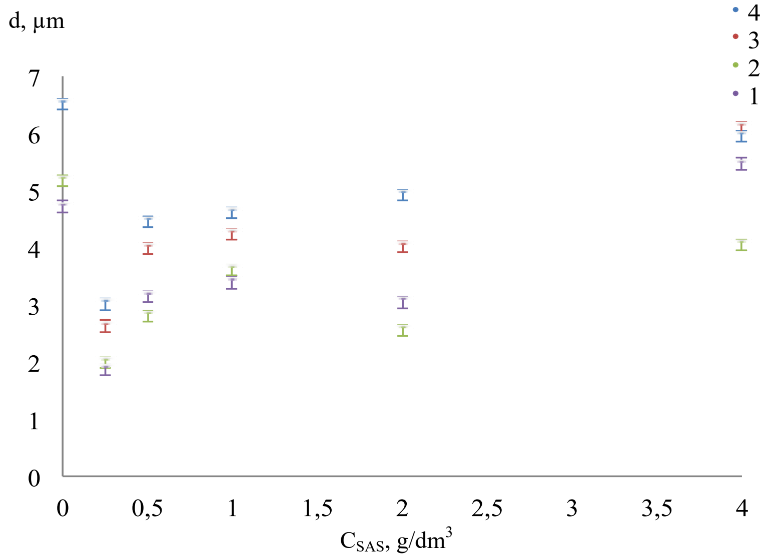
However, at a further increase in the acryl content, there is a tendency to reduce the rate of stabilization. An increase in the concentration of a film-forming agent by 10 times (from 0.5 to 5 g/dm^3) decreases the sedimentation rate only by 5.5 times (V=0.38·10$^{-3.0}$). This is three times less than the effect observed at the introduction of 0.5 g/dm^3 of acryl (Fig. 4, curve 1, C_{SAS}=0). The effect of stabilization of solid-phase pigment dispersions in suspensions in the absence of surfactants limits the process of association of macromolecules. This effect increases at an increase in the concentration of a film-forming agent. At the same time, the number of macromolecules associated directly with the solid surface decreases, since only some segments of molecules from associates are fixed on it. This is evidenced by a consistent decrease in adsorption values (from 0.050 to 0.045 g/g), despite an increase in the content of film-forming agents in water (Fig. 5). As a result, the intensity of disaggregation processes gradually weakens. At the transition of the concentration of a film-forming agent from 0.5 to 5 g/dm^3, the values of the average diameter of particles gradually increase from 4.71 to 6.51 µm (Fig. 5) and larger aggregates settle faster (Fig. 4).

The minimum sedimentation rate of titanium dioxide dispersions at a dosage of 0.25 g/dm^3 of PAN was at the level of 0.097 g/s for any acryl content (Cff=0.5÷5 g/dm^3) in suspensions (Fig. 4, *a*). With the introduction of the same concentration (C_{SAS}=0.25 g/dm^3) of another type of amphiphilic compound PES (Fig. 4, *b*), a decrease in the sedimentation rate to 0.053 g/s in suspensions with a limited acrylic content (C≤1 g/dm^3) was recorded. However, with a further increase in the concentration of film-forming agent (C>1 g/dm^3) in suspensions, sedimentation stability decreased, which reflects an increase in the deposition rate of TiO_2 to 0.110·10^{-3} g/s at Cff=5.0 g/dm^3.

The reason for the change in the influence of PES on the stability of suspensions at an increase in the concentration of the film-forming agent is possible to understand by making a comparative analysis with the values of the average diameter of particles in isoconcentration suspensions (Fig. 6). In aqueous-acrylic suspensions with the content of a film-forming agent of 0.5 to 1 g/dm^3, the minimum d_{av} was 2.64÷3.1 µm (C_{SAS}=0.25 g/dm^3). Further concentration of acryl (Cff==4÷5 g/dm^3) at the same dose of PES was accompanied by an increase in the average particle size up to 4.30÷4.61 µm. Unlike PES, in all suspensions, the maximum of wedging activity of PAN (C_{SAS}=0.25 g/dm^3) corresponds to the same minimum of the average diameter (2–3 µm). The independence of PAN on the content of a film-forming agent in suspensions clearly demonstrates the proximity of its adsorption indicators at the same concentration of surfactants both in water-acrylic suspensions (Fig. 7), and in water (Fig. 3).

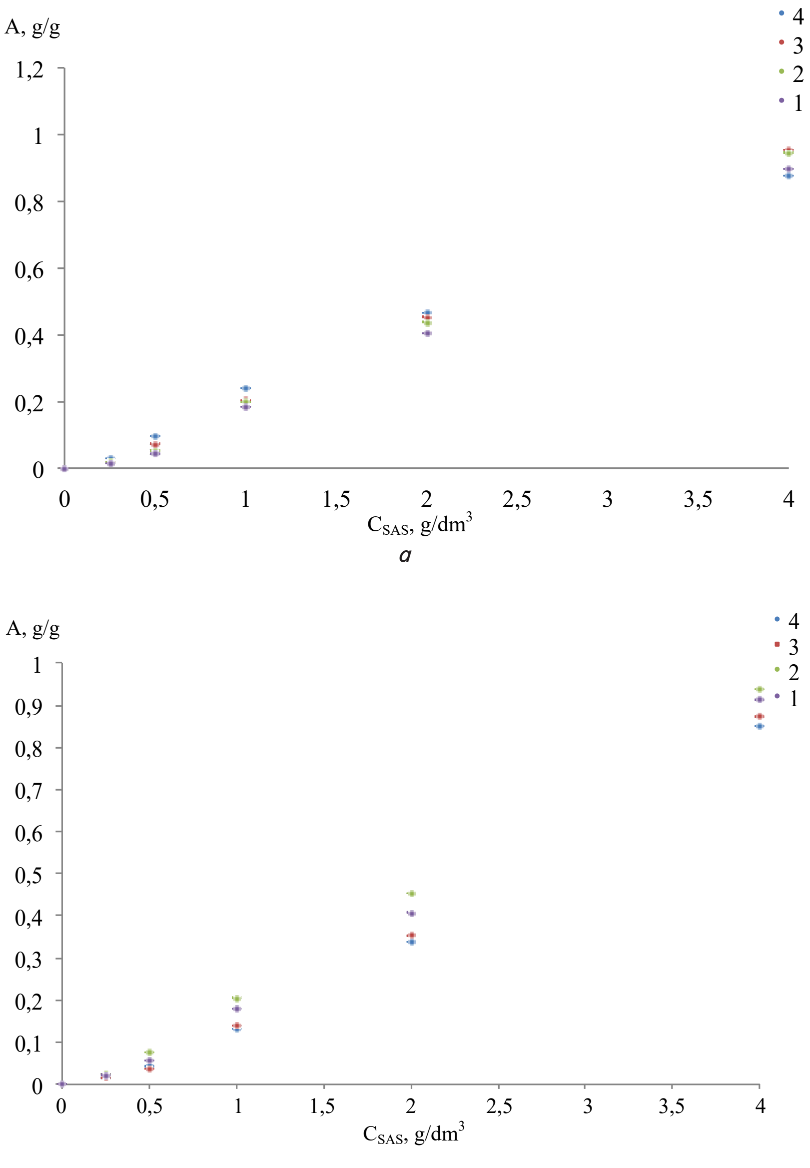


a



b

Fig. 6. Change in the average diameter of pigment particles in the presence of surfactants with the content of film-forming agent in the *Cff* system: 1 – 0.5 g/dm^3; 2 – 1 g/dm^3; 3 – 4 g/dm^3; 4 – 5 g/dm^3; *a* — sodium polyacrylate; *b* — polyether siloxane copolymer



a

b

Fig. 7. Isotherms (T=298 K) of adsorption in the presence of surfactants at the content in the film-forming system: 1 – 0.5 g/dm^3; 2 – 1 g/dm^3; 3 – 4 g/dm^3; 4 – 5 g/dm^3: *a* — sodium polyacrylate; *b* — polyether siloxane copolymer

This indicates the lack of competitive adsorption between the polymer and introduced surfactants, that is, PAN is absorbed on the active areas of the pigment surface free of film-forming macromolecules. A decrease in the magnitude of dispersed processes of titanium dioxide in the presence of PES and, as a result, sedimentation stability in concentrated water-acrylic suspensions is associated with a decrease in adsorption of polyether siloxane copolymer. At an increase in the content of a film-forming agent in water ($Cff \geq 1$ g/dm^3), that is, as the pigment surface was blocked by acryl, the adsorption value of PES on the pigment decreased from 0.025 to 0.015 g/dm^3.

6. Discussion of the results of sedimentation and dispersing effects of SAS

In the compositions "water-SAS-TiO$_2$", the maximum stabilizing activity of both additives was recorded at their content in the suspension at the level of 1.0 g/dm^3, which is evidenced by changes in the rate of sedimentation of surfactants in aqueous suspensions, shown in Fig. 1. PAN has the highest stabilizing effect (Fig. 1, curve *a*). At an increase in its content in suspensions from 0 to 1.0 g/dm^3, the sedimentation rate decreased by 53.2 times (relative to water without surfactants) and amounted to $0.039 \cdot 10^{-3}$ g/s. PES at the same concentration area (Fig. 1, curve *b*) shows a decrease in the rate of sedimentation of pigment particles to $0.112 \cdot 10^{-3}$ g/s, that is, the effect of this surfactant is by 3.0 times less than that of PAN.

In the "film-forming agent – TiO$_2$" system, the sedimentation rate of pigment particles decreased by 5.52–15.0 times as the acryl content increased (from 0 to 5 g/dm^3). When both PAN (Fig. 4, *a*) and PES (Fig. 4, *b*) were introduced to this system, an additional increase in sedimentation stability of suspensions in a narrow region of their concentrations ($C_{SAS}<0.25$ g/dm^3) was observed. PES (C_{SAS}= =0.25 g/dm^3) reduces the rate of sedimentation of water-acrylic suspensions by 3.2 times. In the case of PAN application, the stabilization effect increases as the content of the film-forming agent in the system increases. Thus, at a film-forming content of 0.5 to 1.0 g/dm^3, the sedimentation rate decreased by 1.6 times and amounted to V=0.097÷0.098 g/s (Fig. 4, *a*). At the further concentration of the film-forming agent in the system (Cff>1.0 g/dm^3), the stabilizing activity of PAN increased by 2.4 times and the sedimentation rate was V=0.089÷0.098 g/s (Fig. 4, *a*).

The nature of the change in the stabilizing activity of surfactants is explained within the framework of the established regularity of the development of the processes of disaggregation of solid-phase pigment particles.

In the compositions "water-surfactant-TiO$_2$", the maximum disaggregating effect of the introduced surfactants (Fig. 2, curves *a* and *b*) was recorded at the same concentration, in which the maximum stabilizing activity was observed (C_{SAS}=1 g/dm^3). The average diameter decreased by 8.86 µm (PES) and by 9.65 µm (PAN) compared to unmodified aqueous suspension (d=13.12 µm).

In the "film-forming agent-TiO$_2$" system, the average diameter decreased by 2.65 times and amounted to 4.95 µm in the region of small concentrations of film-forming agents (from 0.5 to 1 g/dm^3). In the field of elevated concentrations (Cff>1 g/dm^3), there was a decrease in the dispersing effect of the film-forming agent. The average diameter of pigment particles in comparison with aqueous suspensions decreased only by 1.97 times and made up 6.65 µm. The introduction of both additives into this system (Fig. 6, *a, b*) intensifies the processes of dispersion of pigment particles. The maximum dispersing activity in aqueous-acrylic suspensions was detected at the same concentration as the maximum stabilizing effect (C_{SAS}=0.25 g/dm^3). PES in aqueous-acrylic suspensions (C_{SAS}=0.25 g/dm^3) reduces the average diameter of pigment particles by 1.84 times, d_{av}=3.16 µm (Fig. 6, *b*). In the case of PAN application, the disaggregating effect is more active and increases by 2.54 times, the average diameter is 2.36 µm (Fig. 6, *a*). Thus, the disaggregating effect of PAN prevails (in comparison with PES) in water-acrylic suspensions and correlates with quantitative indicators of sedimentation of pigment particles.

Unlike PES, the maximum of wedging activity of PAN (C_{SAS}=0.25 g/dm^3) in all suspensions corresponds to the same minimum of average diameter (2–3 µm). The independence of PAN on the content of a film-forming agent in suspensions clearly demonstrates the proximity of its adsorption indicators at the same concentration of surfactants, both in water-acrylic suspensions (Fig. 7) and in water (Fig. 3). This indicates the lack of competitive adsorption between the polymer and introduced surfactants, that is, PAN is absorbed on the active areas of the pigment surface free of film-forming macromolecules. A decrease in the value of dispersive processes of titanium dioxide in the presence of PES and, as a result, sedimentation stability in concentrated water-acrylic suspensions is associated with a decrease in the adsorption of the polyether siloxane copolymer. With an increase in the content of film-forming agents in water (Cff≥1 g/dm^3), that is, as the pigment surface was blocked by acryl, the value of PES adsorption on the pigment decreased from 0.025 to 0.015 g/dm^3.

To substantiate the greater disaggregating and stabilizing effect of PAN in comparison with PES, additional studies of adsorption processes at different temperature modes are needed. This will establish a mechanism for fixing surfactants on the surface of the pigment (chemisorption or physical adsorption). The surfactants, which are fixed on the surface of the pigment by chemisorption, are known to have the greatest disaggregating effect [22]. At the same time, reliable stabilization is achieved during the formation of an interfacial adsorption-solvate layer of macromolecules of a film-forming agent and surfactants.

The merit of this study in comparison with papers [23, 24] is the method for measuring the size of suspension particles. This paper uses computer-optical microscopy, which is a direct and informative method for studying the size of solid-phase particles in suspensions. It makes it possible to obtain photos of suspensions and calculate both the average diameter of particles and their fractional composition. This method is perfectly combined with viscometrical and adsorption studies, which was demonstrated in this research. In study [23], the method of dynamic light scattering (which is indirect) was used to determine the size of titanium dioxide particles and to calculate sedimentation rate. In paper [24], indirect methods of estimating the size of particles in suspensions were also used.

In this study, two different additives were compared, for a broader understanding of the mechanism of their action in this system, it is necessary to increase the number of surfactants. To fully understand the mechanism of action of the considered SAS on the sedimentation stability of suspensions, it is necessary to explore their effect on the wettability of titanium dioxide. A logical continuation of this study is to explore the effect of the considered additives on the wettability of titanium dioxide. In addition, it would be interesting to study the effect of additives on the protective, physical, mechanical, and decorative properties of paint and varnish coatings.

7. Conclusions

1. The effect of stabilization of titanium dioxide dispersions in water-acrylic compositions is an additive magnitude determined by the contribution of a film-forming agent and surfactant.
2. Sedimentation processes are determined by the adsorption-wedging action of surfactants, which, in turn, vary, depending on the concentration of acryl and introduced additives.
3. PES and PAN are effective stabilizing and dispersing surfactants, which makes it possible to obtain sedimentation-resistant compositions without delamination and precipitation at their dosed consumption. It was proved that the sedimentation rate at the introduction of additives significantly decreased and reached the minimum value. Lamination is reduced to zero due to an increase in dispersion processes.
4. In the formulations of water-acrylic dispersions, it is recommended to introduce 0.25 g/dm^3 of surfactants, which provide a decrease in sedimentation by 3.5÷3.9 times in comparison with unmodified suspensions.

Acknowledgment

This research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP08856284).

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