

## ANNOTATION

for the dissertation for the degree of Doctor of Philosophy (PhD)  
«8D072100 - Chemical Technology of Organic Substances»

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### **DEVELOPMENT OF MODIFIED WATER-ACRYL COMPOSITES WITH IMPROVED PROTECTIVE AND DECORATIVE PROPERTIES**

#### **Relevance of the topic.**

The rapid progress of water-dispersion paints and varnishes from the group of water-borne ones is due to a number of their advantages compared to other environmentally friendly paints and varnishes. They provide the possibility of low-temperature drying up to room temperature, allow, in contrast to them, as well as materials with a high dry residue, to completely eliminate the use of organic solvents.

In the paint and varnish industry, the most common primary dispersions obtained by emulsion polymerization (WD-PVC). As a result of emulsion polymerization, in contrast to polymerization in solution (secondary dispersion), polymer macromolecules are obtained contained inside the particles of the dispersed phase. This makes it possible to use high-molecular-weight polymers as film formers for high-pressure coatings, which cannot be used in the form of solutions due to their high viscosity. Aqueous dispersions of acrylic copolymers, acrylstyrene copolymers, vinyl acetate homo- and copolymers predominate in coatings formulations. Acrylic coatings are practically transparent to ultraviolet rays; therefore, 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 their luster during prolonged atmospheric exposure. However, despite the advantages of acrylic coatings, they, as, indeed, any water-borne coatings, are inferior to solvent-based ones in terms of anti-corrosion properties.

The implementation of a uniform distribution of pigment particles can be achieved by ensuring the sedimentation stability of the system before the start of polymerization. The conditions for the uniform distribution of the pigment are determined primarily by the colloid-chemical properties of the system, namely, the dispersion and polydispersity of the pigment particles, the state of its surface, sedimentation and aggregation stability. One of the main methods of targeted regulation of the properties of polymer composite materials and coatings is the use of surface-active substances (surfactants). As a result of adsorption phenomena, their physical (and sometimes chemical) interaction with the surface of dispersed particles and the substrate, association with film-forming molecules, the deformation-strength, insulating, adhesive, coloristic and other properties of paint and varnish coatings can significantly change. Despite the large number of works devoted to the study of the effect of surfactants on the properties of composite

polymeric materials, the effect of polymeric surfactants on the process of distribution of solid-phase pigment particles in a paint composition, in particular, 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.

### **Purpose of the study.**

Study of the patterns of modification by polymeric surfactants (polyethersiloxane copolymer, sodium polyacrylate) of water-acrylic compositions with solid-phase pigment particles (titanium dioxide) and the development of effective composite materials with improved protective and decorative properties.

### **Research objectives.**

1. Study of the physicochemical properties of the model systems «H<sub>2</sub>O-surfactant», «H<sub>2</sub>O-surfactant-film-forming», «H<sub>2</sub>O-surfactant-film-forming-pigment», the individual components of which are acrylic lacquer, inorganic pigment titanium dioxide, additives based on sodium polyacrylate and a polyestersiloxane copolymer.

2. Evaluation of the influence of regime parameters and compositions of compositions on the distribution of surfactants, the corresponding changes in energy at the interfacial boundaries of the film-forming agents with air, steel substrate, pigments, as well as on the development of wetting processes, disaggregation of pigment particles and sedimentation stability of compositions.

3. Development of generalizing multifactorial models, solving on their basis the problems of optimizing, predicting target thermodynamic functions (surface energy, surfactant adsorption, wetting, adhesion, dispersion of pigments) depending on the quantitative and qualitative composition of multicomponent systems and other factors, as well as on their complex interface with technological characteristics.

4. Study of the technological characteristics of suspensions, structural-mechanical and protective-decorative properties of films of water-dispersion acrylic paints and varnishes modified with surfactants.

### **Research methods.**

Used certified chemical and instrumental methods of analysis of infrared spectroscopy, viscometry and sedimentation. The surface activity of the studied additives was evaluated based on the measurement of the surface tension ( $\sigma$ , mJ/m<sup>2</sup>) of their solutions (the Dew-Nooy method). The maximum pull-off force of the ring was measured using a tensiometer under isothermal conditions (T=298K). The influence of surfactants on the wetting of titanium dioxide in water-dispersion paints and varnishes based on acrylic film-forming was evaluated by the criterion of the contact angle of wetting ( $\theta^\circ$ ). The  $\theta$  measurement was carried out using an automatic dynamic contact angle measuring system of the ACAM series. The influence of the concentration regimes of the film-forming and surfactant on the sedimentation stability of titanium dioxide suspensions was determined by the gravimetric method, the essence of which was the periodic weighing of the sediment collected on the cup of a torsion balance (VT-500 brand). When processing experimental data, optimizing compositions (materials) and

technological regimes, methods of mathematical statistics, probabilistic-deterministic planning, as well as a package of ready-made and specially developed author's programs were used. The assessment of structural-mechanical, anticorrosive and decorative characteristics of insulating coatings on a steel substrate was carried out according to standardized methods. The corrosion rate was determined by the gravimetric method (weighing plates before and after soaking in a 10% sulfuric acid solution). The adhesion of the coatings to the steel substrate was evaluated according to ISO 11845:2020 (en). The gloss of the coatings was determined in accordance with the ISO 2813:1994 standard on a BF5–60/60 gloss meter.

**Scientific provisions submitted for defense:**

1. The results of the physicochemical properties of the model systems "H<sub>2</sub>O-surfactant", "H<sub>2</sub>O-surfactant-film-forming", "H<sub>2</sub>O-surfactant-film-forming-pigment", the individual components of which are acrylic lacquer, inorganic pigment titanium dioxide, additives based on sodium polyacrylate and a polyestersiloxane copolymer.

2. Results of studying the influence of operating parameters and compositions of compositions on the parameters of surfactant distribution, the corresponding changes in energy at the interfacial boundaries of the film-forming agents with air, steel substrate, pigment, the development of wetting processes, disaggregation of pigment particles and sedimentation stability of compositions.

3. 3. Data of generalizing multifactorial models, solving on their basis the problems of optimizing, predicting target thermodynamic functions (surface energy, surfactant adsorption, wetting, adhesion, dispersion of pigments) depending on the quantitative and qualitative composition of multicomponent systems and other factors, as well as on their complex interface with technological characteristics.

4. Results of the study of technological characteristics of suspensions, structural-mechanical and protective-decorative properties of films of water-dispersion acrylic paints and varnishes modified with surfactants.

**Scientific novelty.**

The possibility of using a polyethersiloxane copolymer and sodium polyacrylate in paint and varnish compositions based on an aqueous dispersion of an acrylic polymer and titanium dioxide as modifiers with a dispersing effect has been proven. Sodium polyacrylate is a surfactant that concentrates at the water-air interface. Polyethersiloxane copolymer is a weaker surface-active additive than PAN, which is explained by a lower content of ionized forms in isoconcentration solutions. It has been experimentally proven that in water-acrylic suspensions that are isoconcentrated in terms of surfactant content, the surface activity of PAN exceeds PES from 6.4 to 4.5 times as the content of the film-forming agent increases from 10 to 30%. Based on the method of probabilistically determined planning, equations are derived for calculating the contact angle of wetting of titanium dioxide and steel, depending on the content of the film-forming agent and surfactant. A narrow range of concentrations of two types of surfactants providing the maximum characteristics of wedging and disaggregation of pigment particles

was revealed. Sodium polyacrylate, which provides more adsorption strength reduction, exhibits a greater dispersing effect than polyethersiloxane copolymer. The maximum disaggregation effect for PAN and PES at the same concentration of surfactant (surfactant=0.25 g/dm<sup>3</sup>) and PES (0.010 g/g). Generalized models and, based on them, nomograms have been developed to determine the degree of pigment dispersion from the quantitative contents of PAN and PES film-forming and additives in water-acrylic compositions. It has been proven that the settling rate when adding additives significantly decreased and reached the minimum value. Stratification is reduced to zero due to an increase in dispersion processes. The introduction of surfactants into acrylic-containing compositions increases the work of adhesion of WD-PVC solutions on a steel substrate. A close correlation was found between the performance of adhesion and the adhesion of modified compositions on a steel substrate.

**The validity and reliability of scientific provisions,** results and recommendations are based on the use of standard proven methods and research methods, the use of physical and chemical laws, the high convergence of the results of theoretical and experimental data, using methods of statistical processing of experimental results with a high correlation index.

**The practical significance of the work.**

It consists in the development of new modified compositions of coatings, which can be used for decorative and protective treatment of various coatings.

**Personal contribution of the author.**

It consists in formulating and substantiating the topic of dissertation research, setting tasks, and conducting theoretical and experimental research, formulating scientific positions, proving their novelty, developing methodological support for the work carried out, developing conclusions and recommendations.

**Approbation of work.**

The results of research on the dissertation were reported and approved at international scientific and practical conferences: «Chemistry, Physics, Mathematics: Theoretical and Applied Research, Moscow, Internauka,» Study of the dispersive effect of polyethersiloxane copolymer in water-dispersion systems.

3rd international Conference on Polymer Science and Composite Materials, Rome, Italy, 2022, «Study of the adsorption processes of pigment aggregates under the action of surfactants in water-acrylic paints».

**Publications.**

During the doctoral studies, 8 co-authored papers were published, including 4 articles in journals peer-reviewed on the Scopus database, Web of Science with high Q1-Q3 quartiles; 2 articles in journals recommended by the Education and Science Control Committee of the Ministry of Science and Higher Education; 2 reports at International scientific and practical conferences.

**Contribution of the dissertation student to the preparation of publications**

1. "Investigation of the dispersing effect of polymeric surfactants in acrylic dispersions". Selection of materials for the review, writing a review and

introduction, processing and description of the results of experiments, writing a conclusion.

2 "The use of computer-microoptical method for the analysis of the dispersing effect of polymer modifiers". Search for publications for a review and its writing, writing sections: research methodology, research results, design of graphs, responses to reviewers' comments.

3 "Optimization of pigment and filler disaggregation processes using probabilistic-deterministic modeling techniques". Section writing: introduction, research methodology, mathematical processing and discussion of experimental results, article design.

4 "Development of sedimentation resistant water-acrylic titanium dioxide dispersions". Selection of materials for the review and its writing, writing an introduction, methods and conclusions, preparation of graphs and their description, article design.

6 "Modeling the wetting of titanium dioxide and steel substrate in water-borne paint and varnish materials in the presence of surfactants". Drawing up an article plan, writing sections: discussion of research results and conclusions, article design

6. Exploration of the adsorption reduction of the pigment aggregates strength under the effect of surfactants in water-dispersion paints. Writing sections: introduction, methodology, experiments and their results, article design.

7. "Investigation of the dispersing effect of polyethersiloxane copolymer in water-dispersion systems". Development of a report plan, selection of materials, writing the main part with a discussion of the research results.

8. "Study of the adsorption processes of pigment aggregates under the action of surfactants in water-acrylic paints". Development of a report plan, selection and systematization of materials, writing two sections, presentation at a conference.

### **The structure and scope of the dissertation.**

The dissertation consists of an introduction, 6 chapters, a conclusion, a list of references, contains 52 figures, 12 tables, a list of references includes 111 titles of works by domestic and foreign authors.

**The introduction** presents the scientific apparatus of the study, the rationale for the relevance of the study, the degree of its study in theory and practice, defines the goal, objectives, object and subject of research, reveals the scientific novelty, theoretical and practical significance of the work, defines research methods.

**Section 1** includes an analysis of the state, problems and promising areas of application of water-dispersion paints and varnishes, protective and decorative properties of water-borne paints and varnishes, modernization of coatings formulations based on the use of new film formers and pigments, modern trends in modifying paints and varnishes.

**Section 2** includes studies of the physicochemical and surface-active properties of polymer amphiphilic compounds differing in molecular weight composition and functional groups (volumetric properties of aqueous solutions of additives, surface properties of amphiphilic compounds at the water-air interface,

surface properties of amphiphilic compounds at the interphase boundary "solid-air").

**Section 3** presents the results of a study of the effect of surfactants on the wetting of titanium dioxide in water-dispersion paints and varnishes based on an acrylic film-forming agent, as well as modeling the combined effect of surfactant concentration and film-forming agent on the wetting ability of water-acrylic compositions.

**Section 4** includes studies of the dispersing effect of additives in aqueous and acrylic suspensions of titanium dioxide, optimization of the compositions of paints and varnishes.

**Section 5** presents studies on the stabilizing effect of two types of amphiphilic polymer compounds (polyethersiloxane copolymer, sodium polyacrylate) in water-acrylic compositions with rutile titanium dioxide.

**Section 6** includes studies of the structural-mechanical and anti-corrosion properties of water-dispersion acrylic compositions.

In conclusion, the results of the study are summarized, the main conclusions are formulated, confirming and proving the truth of the provisions submitted for defense.

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