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MODERN APPROACHES TO THE USE OF MODIFIERS IN WATER-ACRYLIC FILM-FORMING SYSTEMS

Abctract: *Acrylic water-dispersion coatings occupy a significant place in the market due to their environmental friendliness, technological flexibility and versatility of application. However, in order to ensure stable performance characteristics such as adhesion, strength, elasticity and resistance to external influences, targeted modification of formulation compositions is necessary. The use of modifiers makes it possible to adapt the properties of compositions to the specific conditions of application and operation, as well as to ensure high-quality paintwork. This article provides an overview of existing approaches to the use of modifiers in water-acrylic film-forming compositions and their effect on the properties of finished coatings. The purpose of the article is to systematize data on the use of modifying additives in acrylic aqueous dispersions, analyze their functional purpose, and evaluate the impact on the technological and operational characteristics of coatings. Conclusion. The review identifies current trends in the development and application of modifiers in acrylic water-dispersion systems, emphasizing the need for further research to optimize formulations, improve component compatibility, and develop new highly effective additives.*

Key words: *acrylic film-forming agents, modifiers, paint and varnish materials, dispersants, water-dispersion compositions.*

Introduction

Modern water-based paints and varnishes, in particular acrylic water-dispersion coatings, occupy a significant market share due to their environmental friendliness, technological flexibility and a wide range of applications, reducing fire and explosion hazards and physiological risks for consumers [1, 2]. However, along with the advantages such as safety, ease of handling and low toxicity, Water-dispersion coatings have a number of disadvantages. In particular, compared with organo-dilutable analogues, they are inferior in water resistance, adhesion and corrosion resistance [3]. In addition, there is an increasing need to develop universal formulations that would ensure not only environmental friendliness, but also stability of characteristics under different climatic conditions and on different types of substrates. At the same time, the obtained coatings should remain competitive in comparison with alternative options in terms of cost and availability [4, 5]. The introduction of modifying additives makes it possible to purposefully improve the decorative and operational properties of paint and varnish materials [6].

General information about water-acrylic systems

According to world experience [7], aqueous dispersions of acrylic copolymers, acrylic styrene copolymers, homo- and vinyl acetate copolymers predominate in Water-dispersion paint formulations. Water-based acrylic latexes are two-phase systems in which polymer particles are dispersed in a continuous aqueous phase. The widespread use of acrylic latexes is explained by their cost-effectiveness and universal properties, which can be achieved by selecting the composition of the monomer [8]. Acrylic coatings are practically transparent to ultraviolet rays, therefore, the processes of destruction of the film-forming agent in them occur much more slowly, as a result of which they are not prone to yellowing and retain their luster under prolonged atmospheric exposure [9].

Film formation in water-acrylic systems is carried out due to the coalescence of polymer particles occurring during evaporation of the dispersion medium – water (Fig. 1). As water is removed, latex particles approach, compact and begin to deform, which leads to their fusion and the formation of a continuous polymer film [10, 11]. For this process to be effective, it is necessary to exceed the minimum film formation temperature (MFFT), a temperature threshold below which coalescence of latex particles either does not occur at all or leads to a defective coating with a porous or loose structure [12].

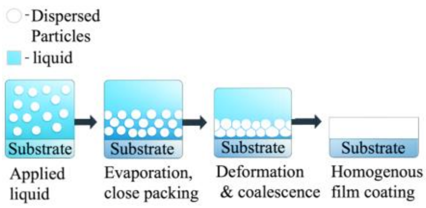

Figure 1 – The process of forming a film of paint and varnish material

MFFT depends on many factors: the chemical nature and T_g (glass transition temperature) of the polymer, the molecular weight, the content of functional and polar groups, the presence and concentration of coalescent additives, as well as the drying conditions – temperature, humidity, ventilation [13, 14]. Unlike organo-dilutable systems, in which film formation occurs due to evaporation of volatile solvents with simultaneous diffusion of polymer chains, in aqueous systems this process has an additional stage of coalescence, sensitive to temperature and mechanical influences [15].

To reduce MFFT and ensure film formation at room temperature, coalescing agents are introduced into the formulations of aqueous coatings – organic compounds capable of temporarily plasticizing the polymer phase, facilitating particle fusion [16]. However, the use of such additives is limited by their volatility, environmental safety, and impact on the final coating properties. In modern research, alternative approaches are actively being considered, including the development of self-film-forming latexes and modification of the surface of polymer particles [17]. Figure 2 shows the origin of the monomers used for the synthesis of acrylic and copolymer latexes used in water-dispersion paints and varnishes [18].

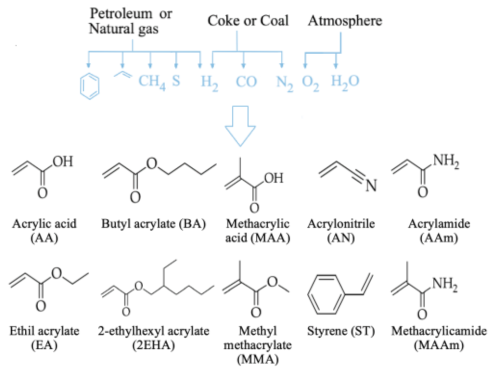

Figure 2 – Chemical structure of acrylic acid

A typical binder is a copolymer of acrylic acids and their derivatives, which forms a stable dispersion in water. The monomers shown in Figure 2 have varying degrees of hydrophobicity, reactivity, and functionality, which makes it possible to obtain polymers with specified properties for specific applications. The use of copolymerization of these monomers makes it possible to control characteristics such as elasticity, adhesion, chemical resistance, water resistance, and glass transition temperature of latexes. The quality of film formation largely depends on the composition of the film-forming agent, the presence of coalescent additives, as well as modifiers. The main properties of coatings, such as elasticity, strength, resistance to UV radiation and water, are determined by the nature and structure of the polymer, the degree of crosslinking, and the interaction of components in the composition [19-21].

Types of modifiers and their mechanisms of action

The choice of modifier governs the service durability of waterborne acrylic coatings because it affects the density of the polymer network, moisture uptake, and resistance to photodegradation. The most pronounced improvement in performance under humid conditions and during wet-dry cycling is typically achieved by crosslinking and post-crosslinking modifiers, such as polyaziridines and carbodiimides, which reduce swelling, increase cohesive film strength, and maintain wet adhesion upon water exposure [22]. Under temperature fluctuations, coalescents and plasticizing agents (e.g., 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, Texanol) enhance flexibility and crack resistance; however, excessive dosages may impair barrier performance by increasing matrix mobility and water permeability. Long-term atmospheric durability under ultraviolet irradiation critically depends on light stabilizers, including benzotriazole- or benzophenone-type UV absorbers and hindered amine light stabilizers (HALS), which suppress radical photo-oxidation and retard binder degradation; in this context, the appropriate selection of modifiers and accelerated weathering protocols is particularly important for waterborne acrylic systems that are sensitive to moisture and aging conditions [23]. According to the literature on waterborne acrylic binders [24], sustained enhancement of mechanical and protective properties is most effectively achieved by combining post-crosslinking with barrier-reinforcing fillers; platelet-type and nanostructured additives, including cellulose nanocrystals, are especially effective because they create a more tortuous diffusion pathway for water and ions and thereby improve barrier and anticorrosion performance.

Consequently, increased durability of waterborne acrylic coatings is attained not through a single additive but through integrated formulation design, in which multiple functional components jointly determine the required processing and in-service film properties. A typical formulation of water-dispersion paints and varnishes contains from three to five, and in some cases more functional additives, the proportion of which is about 1-3% of the total mass of the composition, reaching in some cases 10% or more. Despite their relatively small mass, these additives can form up to 25% of the cost of raw materials and semi-finished products, which emphasizes their importance both from a technological and economic point of view [25]. According to the generally accepted classification, modifying additives are divided into four main categories, covering more than a dozen functional subgroups (Table 1) [26].

As follows from the analysis of modern literature sources, the formation of coatings with high adhesive strength requires both the choice of the appropriate type of film-forming agent and the use of functional modifiers capable of enhancing interfacial interactions. Effective components in this context are polyester, vinyl ether, bisphenol, and epoxy resins, as well as copolymers with a high content of polar fragments [27].

Table 1 – Functions of additives in water-dispersion coatings

Group	Function of additives
A	Regulation of the conditions of production, packaging and storage of paint and varnish compositions
B	Influence on the process of applying paintwork
C	Control of the film formation process
D	Formation and stabilization of the properties of the finished coating

It has been established that a purposeful increase in the proportion of polar functional groups in the polymer structure, such as hydroxyl (–OH), carboxyl (–COOH), amide (–$CONH_2$) and urethane (–CONH), improves the interfacial interaction with the substrate and, as a result, increases adhesion [28]. The adhesive characteristics are influenced not only by the nature of the additives, but also by their concentration, as well as the combined effect of solvents, pigments, fillers and other functional components of the composition, which requires an integrated approach to prescription optimization [29, 30].

Bioadditives are among the promising modifiers used in water-dispersion acrylic film-forming systems [31, 32]. Biopolymers of natural origin, such as chitosan, lignin, alginates and cellulose derivatives (for example, carboxymethylcellulose), are increasingly used due to their versatility and environmental safety. These compounds can be introduced into the structure of the polymer composition in two fundamentally different ways. During physical implementation, they are distributed in the binder volume as a dispersed phase (for example, in the form of particles, droplets or molecular aggregates), without entering into covalent interaction with the polymer matrix. This approach makes it possible to modify the physico-chemical characteristics of the coating due to phase interaction, sorption, or interfacial orientation. In the case of chemical incorporation, modifiers are incorporated into the polymer structure at the synthesis stage through copolymerization, grafting, or crosslinking reactions, which provides a more stable and controlled effect on the level of intermolecular organization and performance properties of coatings such as adhesion, elasticity, and barrier (against the penetration of water, gases, and ions) [33, 34]. In addition, some biopolymers can act as natural coalescers or stabilizers, reducing the need for volatile organic additives [35, 36].

Inorganic modifiers such as titanium dioxide (TiO_2), silicon dioxide (SiO_2), zinc oxide (ZnO), alumina and hexagonal boron nitride are actively used to improve the performance of acrylic coatings. Their introduction into the polymer matrix contributes to the formation of hybrid systems with increased resistance to ultraviolet radiation, abrasive wear, corrosion and microbiological degradation. [37, 38]. At the same time, nanoparticles can simultaneously act as rheological regulators and reinforcing agents, contributing to an increase in the strength, elasticity and adhesion of the coating. Some of them, like TiO_2 and ZnO, also exhibit photocatalytic activity, providing the film's self-cleaning properties when exposed to sunlight.

The necessary additives in the formulations of water-dispersion paints and varnishes are surfactants [39]. They provide a reduction in free energy at the interface of phases and, as a result, lead to stabilization of the system. All water-based coatings require surfactants to create a thermodynamically stable dispersion due to fine regulation of interfacial interactions. They perform a number of critically important functions: they act as emulsifiers in the synthesis of polymer binders, dispersants of pigment particles, improve the wettability of low-energy substrates, prevent defects associated with surface tension gradients, and regulate foaming processes during application [40, 41].

A special class consists of surface-active polymers, such as associative thickeners (HEUR, HASE, etc.), which are used to fine-tune the rheological characteristics of systems, including thixotropy and resistance to runoff [42]. Along with this, anionic polyelectrolytes (for example, polyphosphates and polyacrylates) are widely used in aqueous dispersions as effective dispersing agents that stabilize the pigment-binding boundary [43].

The complexity of water-dispersion paints formulations is due to the competition between various low- and high-molecular weight components for adsorption on surfaces such as binder particles, pigment, and substrate. Typical systems are dominated by anionic and nonionic amphiphilic surfactants, including sulfates of fatty alcohols, alkylaryl sulfonates and ethoxylates of alcohols, due to their versatility and compatibility with acrylic polymers. Cationic and amphoteric surfactants are used much less frequently due to limited compatibility and the risk of coagulation of latex particles [44].

Some specialized surfactants have found application in narrow areas.: Fluorinated compounds (for example, perfluoroalkyl sulfonates) and silicone surfactants can significantly reduce surface tension, up to 20-25 mN/m, eliminating defects associated with uneven drying and coating distribution [45]. Of particular interest are acetylene glycols, surface-active compounds that do not have a pronounced tendency to micelle formation, but are capable of forming ordered monomolecular layers at the phase boundary, characterized by high stability and significant surface pressure. Due to the presence of short and bulky hydrocarbon substituents near the polar group, these compounds exhibit pronounced adsorption properties and effectively stabilize films without collapsing under mechanical or thermal stress. These surfactants are widely used as anti-foaming additives, especially in formulations sensitive to microbubbles and film defects during curing [46].

Adaptive functional additives capable of modifying coating properties in response to changes in external conditions are of particular interest [47, 48]. Such components ensure the stimuli-sensitive behavior of the material. They respond to changes in temperature, humidity, and pH, and may also be sensitive to light or an electric field. The introduction of such additives makes it possible to create coatings with adjustable properties, and in some cases, with the ability to independently restore the structure after damage, such as microcracks or scratches. This is especially important for use in conditions of variable temperatures, high humidity or mechanical stress, where the integrity of the coating may be compromised. Thus, the introduction of thermosensitive copolymers can allow the film to change its permeability at certain temperatures, and pH-sensitive groups can provide controlled adhesion or swelling depending on the acidity of the medium [49].

Methods of introducing modifiers

The methods of introducing modifiers into water-dispersion film-forming compositions significantly affect the distribution of functional components in the polymer matrix, the efficiency of interaction and the stability of the system. In general, two approaches are distinguished: in situ modification, in which additives are introduced at the stage of dispersion synthesis, and post-synthetic modification, when modifiers are added to an already formed system [50].

The in situ method is implemented by co-polymerization of the main monomer and the functional additive in the same reaction medium. This approach ensures a homogeneous distribution of the modifier, increased coating stability, and stronger interfacial bonds between the components. In addition, under certain conditions, the modifier can be covalently integrated into a macromolecular chain, forming a copolymer structure [51].

In the post-synthetic approach, modifiers are introduced after the synthesis of the main binder. This method is convenient from a technological point of view, as it allows you to quickly adjust the properties of the finished composition (viscosity, thixotropy, wettability, UV resistance) without changing the polymer structure. However, if there is insufficient compatibility or high viscosity, additive aggregation or phase separation may occur [52].

Alternative methods for obtaining dispersions include the phase inversion method, in which a pre-synthesized polymer is dissolved in an organic solvent and then converted to an aqueous phase to form latex [53-56].

Mini-emulsion polymerization provides a narrower particle distribution and increased inclusion of hydrophobic additives. In Pickering dispersion, latex particles are stabilized not by traditional surfactants, but by inorganic solid particles (silicon dioxide or titanium oxide), which is especially important for creating coatings with increased thermal and mechanical resistance [57-60].

Comparative characteristics of various types of modifiers in terms of adhesive activity, environmental safety, economic accessibility and functional orientation are presented in Table 2.

The choice of modification method is determined by the purpose of the coating, the compatibility of the components, the required stability of the system, as well as the scale of production. In conditions of large-scale synthesis, the in situ approach is often preferred due to its integration into the technological chain. In laboratory and applied conditions, on the contrary, post-synthetic modification gives more flexibility in the selection of formulations.

Conclusion

Modern approaches to the modification of water-dispersion coatings make it possible to create a new generation of coatings with improved properties. The development of surface engineering, modeling, and biomodification technologies opens up broad prospects for sustainable development in the paint and varnish industry. At the same time, further fundamental study of the mechanisms of interaction of the components is required, as well as a systematic approach to standardization, toxicological and environmental assessment of new formulations.

Table 2 – Comparative analysis of the types of water-dispersion paint modifiers

Modifier Type	Adhesion	Environmental Friendliness	Cost	Effects
Surfactants (anionic, nonionic)	Significant, especially for metals	Average – depends on the nature of the surfactant	Low / Average	Stabilization, foam resistance, application comfort
Biopolymers (chitosan, lignin)	Moderate, depends on the substrate	Very high	Average / High	Antimicrobial, biodegradable
Nanoparticles (TiO_2, SiO_2, ZnO, MgO)	Indirect improvement through morphology	Average /High	Average / High	UV protection, mechanical strength
Functional polymers, composites	Targeted increase in adhesion	Average	Average	Adjustable rheology, heat resistance
Complex additives («smart»)	The synergistic effect	From medium to high	Average	Multifunctional, adaptive behavior

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СУ-АКРИЛ ПЛЕНКАЛАРЫН ҚАЛЫПТАСТЫРУ ЖҮЙЕЛЕРІНДЕ МОДИФИКАТОРЛАРДЫ ҚОЛДАНУДЫҢ ЗАМАНАУИ ТӘСІЛДЕРІ

Акрилді су-дисперсиялық жабындар экологиялық таза, технологиялық икемділігі және қолданудың әмбебаптығы арқасында нарықта айтарлықтай орын алады. Дегенмен, адгезия, беріктік, Серпімділік және сыртқы әсерлерге төзімділік сияқты тұрақты өнімділікті қамтамасыз ету үшін рецепт композицияларын мақсатты түрде өзгерту қажет. Модификаторларды қолдану композициялардың қасиеттерін қолдану мен пайдаланудың нақты жағдайларына бейімдеуге, сондай-ақ бояудың жоғары сапасын қамтамасыз етуге мүмкіндік береді. Осы мақалада су-акрил пленкаларын құрайтын композициялар құрамында модификаторларды қолданудың қолданыстағы тәсілдеріне шолу және олардың дайын жабындардың қасиеттеріне әсері ұсынылады. Мақаланың мақсаты акрилді су дисперсияларында модификациялық қоспаларды қолдану туралы деректерді жүйелеу, олардың функционалдық мақсатын талдау, сондай-ақ жабындардың технологиялық және пайдалану сипаттамаларына әсерін бағалау болып табылады. Қорытынды. Шолу акрил су дисперсиялық жүйелерінде модификаторларды әзірлеу мен қолданудың өзекті бағыттарын анықтайды, бұл рецепттерді оңтайландыру, компоненттердің үйлесімділігін арттыру және жаңа жоғары тиімді қоспаларды әзірлеу бойынша қосымша зерттеулер жүргізу қажеттілігін көрсетеді.

Түйін сөздер: *акрил пленкасы, модификаторлар, бояу материалдары, диспергаторлар, су-дисперсиялық композициялар.*

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СОВРЕМЕННЫЕ ПОДХОДЫ К ИСПОЛЬЗОВАНИЮ МОДИФИКАТОРОВ В ВОДНО-АКРИЛОВЫХ ПЛЕНКООБРАЗУЮЩИХ СИСТЕМАХ

Акриловые водно-дисперсионные покрытия, занимают значительное место на рынке благодаря своей экологичности, технологической гибкости и универсальности применения. Однако для обеспечения стабильных эксплуатационных характеристик, таких как адгезия, прочность, эластичность и устойчивость к внешним воздействиям, необходима целенаправленная модификация рецептурных композиций. Использование модификаторов позволяет адаптировать свойства композиций под специфические условия нанесения и эксплуатации, а также обеспечить высокое качество лакокрасочного покрытия. Настоящая статья представляет обзор существующих подходов к применению модификаторов в составе водно-акриловых пленкообразующих композиций и их влияние на свойства готовых покрытий. Целью статьи является систематизация данных о применении модифицирующих добавок в акриловых водных дисперсиях, анализ их функционального назначения, а также оценка влияния на технологические и эксплуатационные характеристики покрытий. Заключение. Обзор выявляет актуальные направления в области разработки и применения модификаторов в акриловых водно-дисперсионных системах, подчёркивая необходимость дальнейших исследований по оптимизации рецептур, повышению совместимости компонентов и разработке новых высокоэффективных добавок.

Ключевые слова: *акриловое пленкообразующее, модификаторы, лакокрасочные материалы, диспергаторы, водно-дисперсионные композиции.*

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PREPARATION AND ANALYSIS OF A BIODEGRADABLE POLYMER COMPOSITION BASED ON THERMOPLASTIC STARCH REINFORCED WITH STEARIC ACID-MODIFIED MICROCRYSTALLINE CELLULOSE

Abstract: *Plastic waste pollution is a global environmental problem. Therefore, the transition to environmentally friendly, biodegradable polymer materials is an urgent challenge for humanity. Thermoplastic starch is one of the most promising alternatives to synthetic polymers due to its availability, biodegradability, and elasticity. However, its limited mechanical strength and poor barrier properties restrict its application in packaging. To address these limitations, cellulose – a rigid and renewable biopolymer – was used as a reinforcing agent and modified with stearic acid to improve hydrophobicity and barrier performance. A TPS/M-MCC composite was prepared via melt mixing and analyzed using tensile testing, water absorption, biodegradability, and dynamic mechanical analysis (DMA). Fourier-transform infrared (FTIR) spectroscopy confirmed the successful surface modification of cellulose. Compared with neat TPS, the composite demonstrated significantly enhanced mechanical strength, reduced water absorption and retained biodegradability. These findings suggest that TPS reinforced with stearic acid-modified cellulose is a promising environmentally friendly alternative to conventional synthetic polymers for packaging applications.*

Key words: *thermoplastic starch, cellulose, stearic acid, polymer composite, packaging materials.*

Introduction

Thermoplastic starch is one of the most widely used alternatives among modern biopolymers. Thermoplastic starch is produced by intensive mixing and heating of starch in the presence of plasticizers. It is biodegradable, non-toxic, cost-effective, and exhibits excellent properties compared to many other natural biodegradable polymers. At present, it is applied in the production of packaging