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A. N. DYURYAGINA, A. A. LUTSENKO

M. Kozybayev North Kazakhstan State University, Petropavlovsk, Republic of Kazakhstan

STUDY OF THE DISPERSING EFFECT PRODUCED BY POLYETHER SILOXANE COPOLYMERS IN WATER-DISPERSION SYSTEMS

Abstract. The study resulted in determining the disaggregating effect produced by polyether siloxane copolymers in binary and ternary systems based on water-acrylic dispersion. It exposed the regularities in characteristic changing specific for the dispersed composition of solid-phase particle suspensions, and on this basis the polyester siloxane copolymer costs were optimized to achieve the maximum dispersing effect. The studies contributed to establishing the possibility of using polyether siloxane copolymers in paint coating compositions based on acrylic polymers and titanium dioxide as the modifying additive that produces dispersing effect.

Key words: dispersion, pigment, water-acrylic dispersion, titanium dioxide, polyether siloxane copolymer, suspension, modifier.

Introduction. The solid ingredient combining process, which includes a pigment with a liquid polymer medium, is very important in the paint coating manufacture since the product technological and paint properties depend on it, as well as many coating performance properties. The main thing in this process is the pigment interaction with the polymer at the interface between the solid and liquid phases, since its intensity determines the solid particle dispersion in the given medium and the nature of the resulting combined “solid phase-polymer” structures that form the subsequent properties specific for real materials. This was established in Academician P.A.Rebinder’s publications addressing the structure formation and physicochemical mechanics of dispersed systems [1-3] and was further developed by his school staff, A.B.Taubman and S.N.Tolstaya [4-6], who studied pigments interacting with polymers at the phase interface for a wide range of model and real objects. An important technological characteristic exhibited by paint coating materials, which determine the coating structural and mechanical properties (coverage, hardness, strength), is the disaggregation degree specific for pigments and fillers [1].

It was found that the pigment particle dispersion, when combined with the polymer, may both improve and worsen (which has been shown in Figure 1 schematically), in addition, it depends on the chemical nature of both components.

The component combination where the solid particle dispersion in the given polymer medium increases, i.e. the aggregates gradually disintegrate to smaller aggregates or even to primary particles, which is shown in figure 1, a), b), c), is considered appropriate. Interacting with one another through the surface-active material interlayers, solid particles form a developed structure where, as in the framework, a secondary structure of the oriented (and hence strengthened) polymer is formed [2].

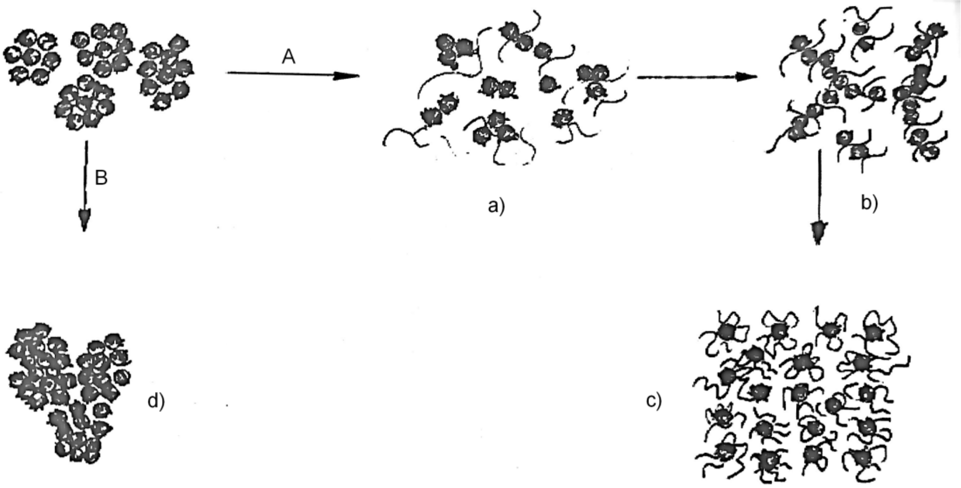

Figure 1 – Change in the pigment dispersion upon its introduction into the polymer medium: A – pigment particle dispersion improvement in comparison with the initial dispersion rate due to natural aggregate peptization: a) separate chain particle formation; b) solid spatial grid formation out of the solid phase particles; c) complete solid particle stabilization. B – pigment dispersion worsening compared with the initial dispersion rate (compact coagulation) – d)

Such combined “solid phase-polymer” structures are called coagulation structures (according to Rebinder); during their formation the system strength increases at the beginning, which is detected by measuring the ultimate statistical shear stress which magnitude is as greater as stronger the solid particle aggregates are peptized in the given medium [7]. Then, after the peptized particles achieve complete stabilization, the strength decreases. Such structures are usually thixotropic, i.e. they are able to recover their physical and mechanical, as well as rheological properties naturally when destructed [3].

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For the overwhelming majority of paint coating materials, when combining a pigment with polymer solutions, it is necessary to form coagulation-type structures, since in this case it is possible to obtain materials and coatings based on them having the necessary properties.

However, in many cases the pigment particle peptization process does not occur naturally, on the contrary, formation of larger aggregates can be observed in comparison with the initial particles, i.e. there is a dispersed phase coagulation process in the given medium, as shown in Fig. 1 b, d. The first process occurs under the liquophilicity of the solid phase particle surface against the liquid medium, and the second one occurs under its liophobicity. For example, hydrophobic graphite is well combined with vegetable oils or non-polar rubbers and disperses well in them, whereas hydrophilic inorganic pigments (ZnO, TiO_2, Fe_2O_3, SiO_2) poorly combine with such hydrocarbon media, which can lead to compact solid phase particle coagulation [3]. In systems with weak and medium interaction, the process where the pigment and the filler combine with the polymer must be intensified. Using surface-active substances (SAS), fine regulators of interface interactions and finished material properties proves to be the most effective method.

The SAS effect is based on forming the surface pigment and filler of the adsorption layer, whose properties, in turn, are determined due to the forming its inner and outer parts. The inner adsorption layer part is formed resulting from the polar SAS group interaction with active surface centers, which promotes peptizing the aggregated pigment and filler particles and the formation of coagulation structure elements. The adsorption layer outer part is formed when hydrocarbon SAS molecule radicals are oriented to the polymer medium, increasing the liquophilicity of the pigment particle surface that is combined with it [2].

Polar hydrophilic pigments introduction into non-polar hydrocarbon media, provides for using modifiers with long hydrocarbon chains (hydrophobisators), for example saturated carboxylic acids, amines or their salts, as well as quaternary ammonium salts and other compounds. When it comes to polar dispersion media, SAS whose molecules contain polar groups in the hydrocarbon radical that are lyophilic with respect to the polymer dispersion medium (i.e., various bifunctional compounds) are used as pigment surface modifiers [2]. This is applicable to all paint coating material types containing polymer solutions as a binder in organic solvents (or in water for water-soluble polymers), water-dispersed binders. Developed and used in recent years polymeric SAS can be even more effective than their low molecular weight analogues due to their high affinity for the polymer medium.

However, the SAS action in paint coating systems is subject to certain physicochemical laws that must be observed for their effective application. An important role in this is played by the polar SAS group nature and the hydrocarbon radical structure specific for their molecules, as well as the polymer chemical nature and the presence of polar functional groups in its molecules. In the paint coating material suspensions, the development of aggregation and disaggregation processes depends both on the surface properties shown by the solid-phase particles and on the quantitative-qualitative composition of the film-forming agents, solvents and surface-active additives. In this connection, it seemed reasonable to evaluate the dispersing effect performance with respect to the polyether siloxane copolymer against the titanium dioxide in the aqueous dispersion of acrylic polymers.

EXPERIMENTAL PART

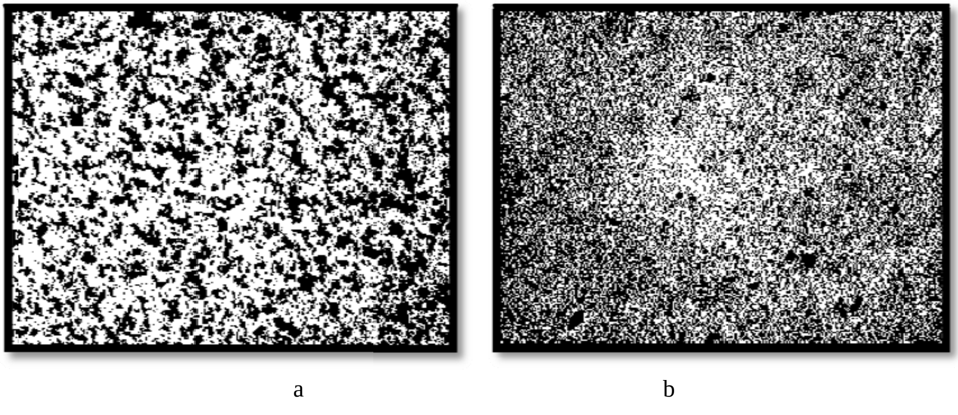
The study included acrylic lacquer as a film-forming agent (TS 2316-014-88753220-2006), water as a solvent and titanium dioxide (P-02) as a pigment. Surface-active additives were used by the brand “Glide 100” (polyether siloxane copolymer).

The quantitative solvent and pigment contents with respect to the suspension weight were set constant at 10% and 1%, respectively, and the modifier consumption varied from 0 to 4 g/dm^3 (by pigment weight). The paint coating material suspensions were prepared at a temperature of 21 °C in a sealed reactor (0.2 dm^3 in volume with a filling factor of 0.60) equipped with a stirring device (impeller agitator with a speed of 300 min^{-1}). The film-forming agent was preliminarily diluted with water, and then a Glide 100 SAS and titanium dioxide were introduced in predetermined amounts with constant stirring. After 10 minutes, a sample was taken with a pneumodosimeter (a drop volume of 0.02 ml). The samples were kept (between the slide and cover glass) under a static load ($P = 30$ g/cm^2) for 5 minutes and subjected to a continuous (along the paint coating material film perimeter) computer-micro-optical scanning [8, 9]. The following quantitative characteristics were determined based on the suspension microanalysis results: the fractional composition (P,%) and the average diameter (d, μm).

RESULTS AND DISCUSSION

Typical titanium dioxide dispersion microimages in water (a) and in the film-forming aqueous solution (b), as well as the corresponding diagrams reflecting the solid-phase particle distribution by the size classes are shown in the figures 1, 2.

Differential curves indicate that the fine fraction content in the solvent (≤44 μm in size) does not exceed 52%. When an acrylic polymer is introduced into water, large aggregates (140 μm) are partially destroyed, which is followed



a b

Figure 1 – Titanium dioxide dispersion microimages at different film-forming agent content. C_{ff}, %: a – 0; b – 10

№	Fractions, mm
1	44
2	63
3	99
4	140
5	198

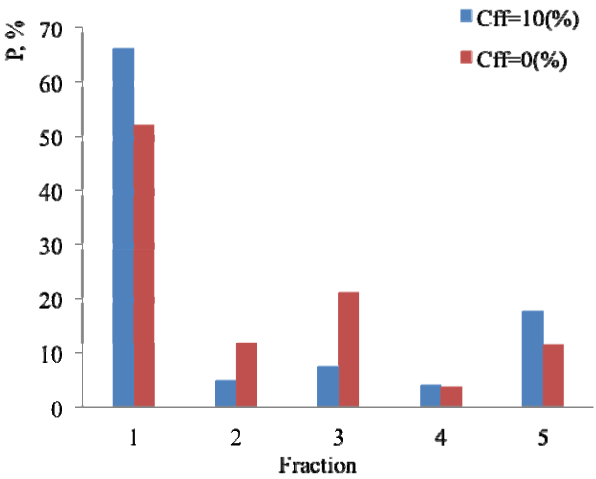


Figure 2 – Differential curves for the particle size distribution of the solid-phase particle fraction in water

by a fine fraction increase to 67%. This process results from the generated disjoining pressure due to the film-forming agent diffusion along the separate particle boundaries; at this stage, the first particles to disaggregate are those bound by point contact mainly and only then those bound by stronger linear and planar contacts [10].

SAS polyether siloxane copolymer introduced into the compositions opens additional possibilities for a purposeful change in the dispersed composition. The depth and direction determined for these changes are shown in figure 3.

In the water-SAS system, the maximum disaggregating effect produced by the modifier was registered when its content stood at 1.0 g/dm^3 (figure 3, curve 1), while the average diameter limit was 4.5 μm. Beyond this concentration section

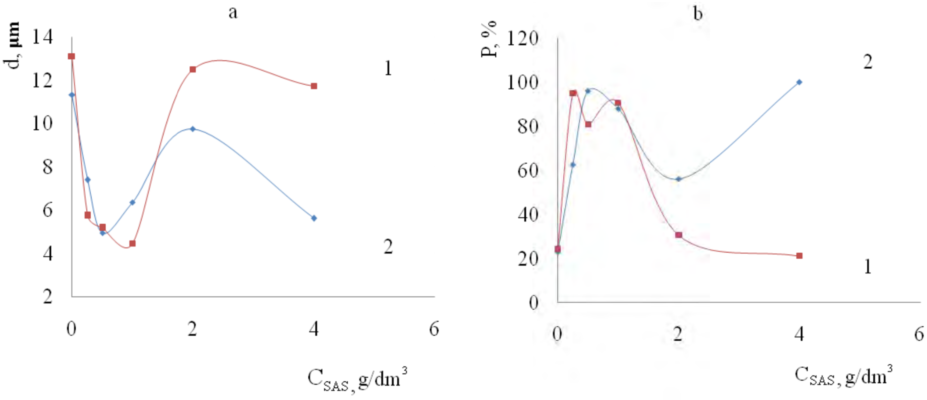


Figure 3 – Changes in the average fine fraction diameter (a) and content (b) depending on the polyether siloxane copolymer concentration

(C_{SAS} > g/dm^3), a secondary aggregation process can be observed, accompanied by an increase in diameter from 4.5 to 12.5 μm and a corresponding reduction in the fine fraction content from 91 to 31%.

Similar patterns in the dispersed composition changes under the influence produced by the polyether siloxane copolymer were also noted in the “film-forming agent-SAS” system: the disaggregating effect in the low concentration region and the flocculation process development with its further concentration. In the first place, we should note the intensity in the film-forming solution (figure 3, curve 2), where the secondary aggregation process is less pronounced than in the water, and secondly, the maximal disaggregating effect is shifted to the lower concentration region ($C_{SAS} \leq 0.5$ g/dm^3).

Conclusion. Comparatively analyzed dispersing effect produced by the modifier under study in binary and ternary systems showed a deeper dispersion in water, which is due to the deficient competition from the side of the film-forming agent macromolecules.

The performed studies let us establish the possibility of using polyether siloxane copolymers in paint coating compositions based on aqueous dispersion of acrylic polymers and titanium dioxide as the modifying additive that produces dispersing effect. The appropriate SAS concentration is its composition content at 0.25 g/dm^3.

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Резюме

А. Н. Дюрягина, А. А. Луценко

ИССЛЕДОВАНИЕ ДИСПЕРГИРУЮЩЕГО ЭФФЕКТА ПОЛИЭФИРСИЛОКСАНОВОГО СОПОЛИМЕРА В ВОДНО-ДИСПЕРСИОННЫХ СИСТЕМАХ

Приведены результаты экспериментальных исследований закономерностей развития процессов дезагрегации диоксида титана в водной дисперсионной среде в присутствии полиэфирсилоксанового сополимера. С помощью приложения компьютерно-микрооптического метода к анализу исследуемых суспензий в автоматическом режиме была установлена закономерность развития процессов агрегации твердофазных пигментов и количественные характеристики их распределения по фракциям.

Ключевые слова: диспергирование, пигмент, водно-акриловая дисперсия, диоксид титана, полиэфирсилоксановый сополимер, суспензия, модификатор.

Резюме

А. Н. Дюрягина, А. А. Луценко

ПОЛИЭФИРСИЛОКСАН СОПОЛИМЕРІНІҢ ҚАТЫСУЫМЕН ТИТАН ДИОКСИДІНІҢ ДИСПЕРСИЯЛЫҚ ҮДЕРІСТЕРІН ЗЕРТТЕУ

Осы жұмыста полиэфирсилоксан сополимерінің қатысуымен су-дисперсиялық ортада титан диоксидін дезаграгациялау үдерістерінің даму заңдылықтарын эксперименталдық зерттеудің нәтижелері келтірілді. Зерттелетін суспензияларды автоматты тәртіпте талдауға қатысты компьютерлік-микрооптикалық әдістің қосымшасының көмегімен қатты фазалық пигменттердің агрегация үдерістерін дамытудың заңнамалығы, оларды фракциялар бойынша бөлудің мөлшерлік сипаттамалары анықталды.

Түін сөздер: дисперсия, пигмент, су-акрил дисперсиясы, титан диоксиді, полиэфирсилоксан сополимері, суспензия, модификатор.