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Physical-Chemical Conditions for Production of Combined Alkyd-Acrylic Dispersion

Eugene A. Indeikin, Olga A. Kulikova, Vladimir B. Manerov

Yaroslavl State Technical University, Yaroslavl Paint Research Institute,
Russia, Yaroslavl, 150044, Polushkina roshcha, 16

Summary: When preparing the mixing of acrylic polymer and copolymer dispersions with alkyd oligomer emulsions it is necessary to provide agregative stability of the combined dispersions. It was established that transfer of polymer particles mass of highly dispersed systems onto particles of less dispersed systems is seen during geterocoagulation of combined dispersions. Optimal physical-chemical and hydrodynamic conditions of the emulsification of alkyd oligomers with the required dispersion degree for producing the mixed systems were established. The combined dispersion stability is determined from the ratio of electrokinetic potentials of particles of polymers and oligomers being combined as well as ratio of their isoelectric points. The zone of dispersion incompatibility was established by method of microelectrophoresis.

Keywords: dispersions, mixing, oligomers, particle size distribution, incompatibility

Introduction

Combining of acrylic polymers dispersions and copolymers with emulsions of alkyd oligomers is used for purposeful regulation of materials' properties on their basis. It allows considerably to improve the adhesion to chalking and earlier painted surfaces, impregnating ability, to increase stability to the influence of the polluting substances, to improve water resistance of the coating. Thus properties, such as fast hardening, hardness of the coating and stability to UV -radiation, caused by presence of acrylic polymers in materials' structure remain. At combining it is necessary to maintain the aggregate stability, i.e. prevention of dispersion system heterocoagulation, both for stability of the material and for maintenance of important properties of the coating.

Heterocoagulation can be caused by various acid-basic character of the particles of the dispersion phase, different charges of the particles. In many cases it can be caused by various particle size distribution of combined dispersion systems.

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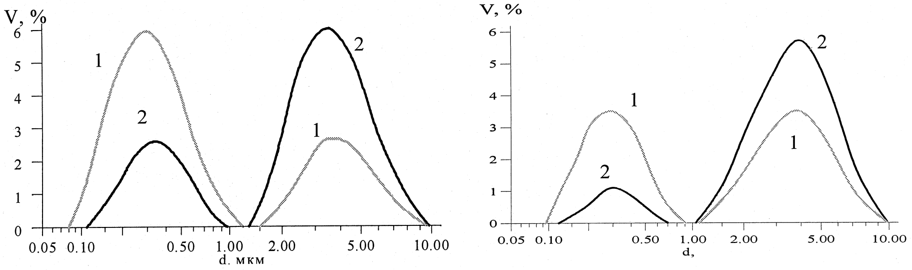
The study of heterocoagulation

By the method of polarized light diffusion is established [1,3], that at combining of dispersions, particles, strongly differing by the sizes, in the ratio of acrylic dispersion (AD): alkyd emulsion (AE) = 70:30, at the initial moment of combining the structure is characterized by a bimodal differential curve distribution (continuous line on the figure 1). In 24 hours the outstripping coagulation of alkyd emulsion is observed (dotted line), which is accompanied by reduction of a maximum appropriate to distribution of acrylic dispersion.

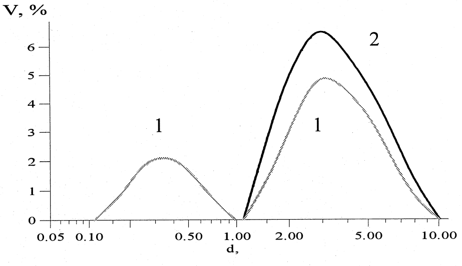
At reduction of a acrylic share in system the acceleration of the process of coagulation, down to complete disappearance of a maximum appropriate to distribution of acrylic dispersion is observed.

At combining of dispersion with smaller distinction at a rate of particles the distribution has an intermediate character in a kind of the greater affinity of two combined dispersions coagulation rates. In case of close on dispersion structure of systems coagulation is not observed.



à) ÀD:AE=70:30

b) ÀD:AE =50:50



c) ÀD:AE =30:70

Figure 1. Differential curve distributions on the sizes of particles mixed dispersions (1 - at the moment of combining; 2 - after 24 hours).

In such a manner there was established, that in process of dispersion heterocoagulation the carry of mass of highly dispersed system polymeric particles on particles of system with smaller dispersity is observed, that defines the final distribution. The necessity of systems close on dispersion structure use for combining is shown.

The conditions of production

We investigate[4] influence of conditions of production on properties of emulsion of alkyd oligomer.

The choice of surfactant for production of the alkyd oligomer emulsions, used for combining with acrylic dispersion is caused as necessary efficiency of emulsifying action in view of the Bankroft law and concept of hydrophilic-lypophilic balance (HLB), and their influence on stability of acrylic dispersions. Thus minimization of surface-active substance in system is important for the declination of their influence on the coating properties. [5]

One of major parameters of the emulsification process is temperature, which influences as on HLB non-ionogenic surfactant according to the equation Griffin-Davis and viscosity of dispersion medium and formed dispersion phase. As have shown our researches [6], at use of anionic emulsifier the average size of the emulsion particles decreases with growth of temperature. Emulsifying ability of alkylphenolethoxylates in the relation to alkyd oligomer grows up to temperature of turbidity with growth of temperature. (Fig. 2).

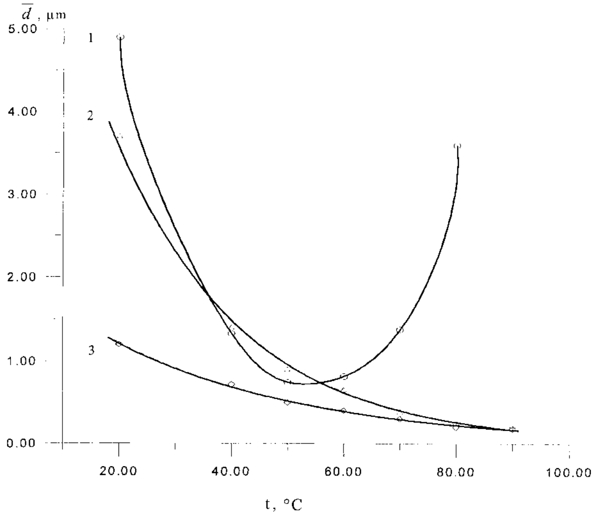


Figure 2. Dependence of the average size of particles on temperature of emulsification for octylphenolethoxylates: 1 - EO = 10; 2 - EO =30; 3 - EO = 40

Probably, it is explained to that the decrease of hydrophility is connected with a smaller degree of oxygen atoms solvation with a simple ether bonds, that causes the increase of the surfactant molecules hydrophobic sites solubility in emulsifying phase with orientation of polar parts into water medium, thus increasing hydrophility of alkyd oligomer.

For surfactant with a ethoxylation degree equal to 10 at achievement of the turbidity point at the expense of temperature increase the sharp decrease of emulsions' dispersity, connected with the beginning of its manipulation is observed. Despite of really high HLB meaning of these surfactants, the manipulation probably is connected with micelle formation of surfactant and with increase of their solubility in alkyd oligomer at the expense of ester, carboxylic and hydroxyl groups presence in it, which promotes surfactant dissolution in them with the meaning of HLB more than 7. The optimum of temperature is higher for emulsifiers with the greater degree of ethoxylation, that is connected to increase of the work, which is necessary for the carry of surfactant molecules from polar medium into non-polar medium with the growth of the ethylene oxide groups contents.

As have shown the results of research, the dependence of alkyd oligomer viscosity from temperature is adequately described by the Eiring equation.

$$\eta = \eta_0 \cdot \exp\frac{\varepsilon}{RT} \qquad (1),$$

where η - viscosity of alkyd oligomer (mPa · s),
η_0 - pre-exponential term which has the dimension of viscosity,
ε- - energy of viscous flow activation (J/mol);
R - universal gas constant, J mol^{-1} Ê$^{-1}$,
Ò - temperature, Ê.

On the basis of the carried out researches on influence of temperature on emulsifying ability of surfactant and rheological properties of alkyd oligomer there was chosen the optimum of emulsifying temperature, which allows to receive emulsions with high dispersity.

We have calculated the average energy of viscous flow activation, which is approximately identical to all considered alkyd oligomers and lies in the interval - 66-68 kJ/mol.

As it can be seen from figure 3, the growth of systems' dispersity with the increase of the surfactant concentration at its certain meaning is sharply slowed down. It is necessary to consider these concentration as expedient, because it is proved to be true also by data on adsorptive titration.

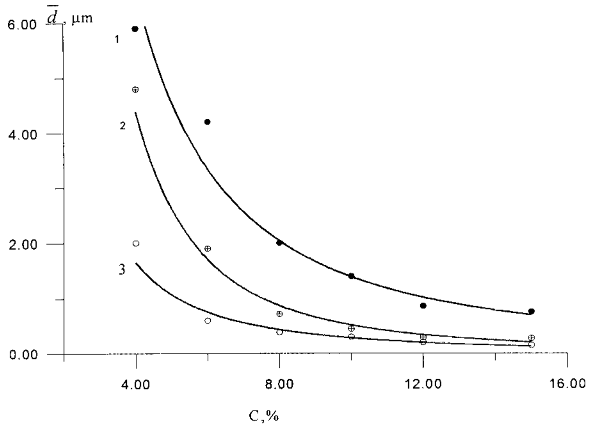


Figure 3. Dependence of the average particle size on concentration (C) of octylphenolethoxylates: 1 - EO = 10; 2 - EO =30; 3 - EO = 40

As have shown our researches, for production of alkyd oligomer emulsions with high dispersion the use of a concentration and temperature phases inversion method is expedient. Thus at the use of non-ionic emulsifier with the greater degree of ethoxylation the concentration inversion comes at the greater concentration of dispersion phase. (fig. 4). Temperature inversion is realized for alkylphenolethoxylates with a degree of ethoxylation equal to 10. ohm

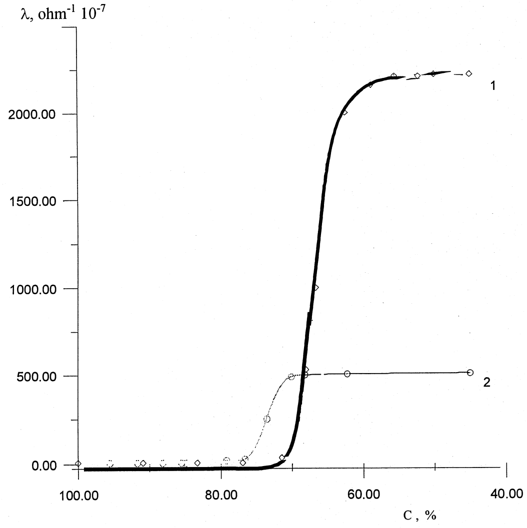


Figure 4. Dependence of electrical conductivity on concentration of dispersion phase for octylphenolethoxylates: 1- EO=10; 2- EO=40

The study of the dispersion phase rheological properties on the size of emulsion particles influence has shown, that dispersity is practically linearly depends on viscosity of alkyd oligomer and can be described by the equation:

$$d = k \cdot \frac{\eta_a}{\eta_c^2}, \qquad (2)$$

Where k - factor which is directly proportional to the surface tension on the interface of the dispersion phase and dispersion medium and inversely proportional to the speed of shift.

Thus on the basis of the carried out researches there were chosen the optimum conditions for the alkyd oligomer emulsification, allowing to receive highly dispersed steady emulsions, which were used in a composition with acrylic dispersions.

Electrokinetic, optical and rheological properties

We investigate physical-chemical properties of combined alkyd-acrylic dispersions, and in particular there was investigated [7] the influence of dispersion media pH value on electrokinetic potential of dispersion phase particles and the meanings of dispersions isoelectric points were established, according to which the zones of dispersion incompatibility were determined.

There is shown, that the meaning of ζ-potentials for acrylic dispersions are determined by presence of anionic surfactant and for the dispersion of acrylate and vinyl acetate copolymer by ionization of carboxyl groups in micelles of polymer. There is determined, that ζ-potential of alkyd emulsion particles, caused depending on pH value by ionization of carboxyl groups or adsorption of neutralizator ions, has a negative mark in a wide range of pH value and does not depend on it dispersity and the type of surfactant.

As it can be seen from the figure 5, there are zones of incompatibility for the acrylic polymer dispersions and alkyd emulsion (**a** and **b**)- the zone of the electrophoretical mobility meanings opposite on a sign, and, hence, of ζ-potential. Besides, this zone is smaller for acrylate and vinyl acetate copolymer and alkyd emulsion, than at pure acrylic dispersion and alkyd emulsion.

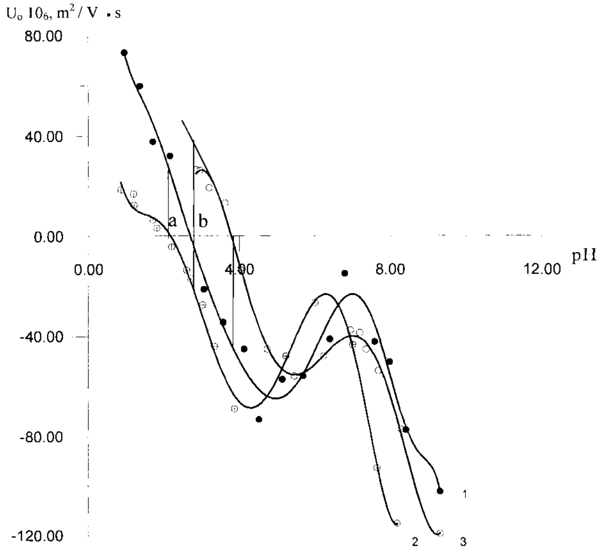


Figure 5. Dependence of electrophoretic mobility U_e of acrylic and alkyd emulsions on pH value 1- alkyd emulsion ; 2- acrylate and vinyl acetate copolymer dispersion; 3- acrylic dispersion.

At the formation of films from the dispersions the zones of incompatibility are equal with zones of increased optical density of polymeric coating (fig. 6).

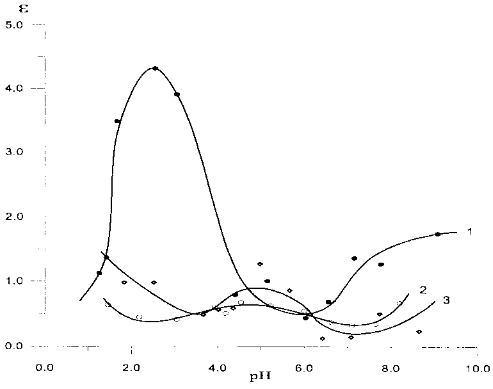


Figure 6. Dependence of film optical density (ε), generated from mixed dispersions from pH: 1- AD + AE ($\bar{d}$=2,6 μm); 2 - AD + AE ($\bar{d}$=0,5 μm); 3 - AD + AE ($\bar{d}$=0,2 μm).

In a case, when the zones of incompatibility are not present, the maxima of optical density are marked in zones ζ-potential negative meaning reduction for alkyd oligomer. Probably, it is connected with the increase of system concentration caused by evaporation of dispersion medium and results in coagulation. Besides, the particles of alkyd oligomer are the coagulation germs of the more highly dispersed acrylic dispersion particles.

The size of dispersion ζ-potential influences on rheological properties of dispersion. It was determined, that for the acrylic polymer and its copolymer with vinyl acetate the increase of viscosity with electrokinetic potential negative meaning growth is observed. Probably, it is connected with increase of diffusion layer thickness and adsorptive-solvative environment, i.e. with the increase of hydrodynamic volume. As against from polymer dispersions the viscosity of alkyd emulsion grows practically monotonously with the ðÍ value growth, that is connected with increase of carboxyl groups ionization.

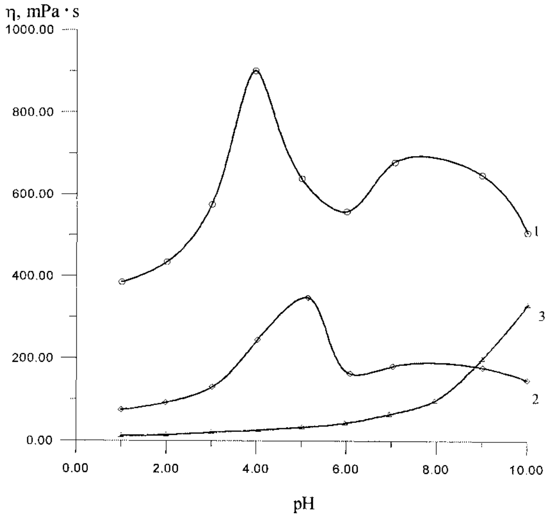


Figure 7. Dependence of dispersions' viscosity from pH:
1. - dispersion of acrylate and vinyl acetate copolymer;
2. - dispersion of acrylate and vinyl acetate copolymer + alkyd emulsion;
3. - alkyd emulsion.

For mixed dispersions as with the use of acrylic polymer and copolymer with vinyl acetate the character of viscosity dependence from ðÍ is kept similar to character of their dependence in absence of alkyd oligomer in system structure (fig. 7).

Thus in the first case the constant absolute meanings of viscosity are kept, in the second case the downturn of acrylate and vinyl acetate copolymer dispersion viscosity is observed and at introduction of alkyd oligomer emulsion in it. Probably, it is connected with change of the particles charge and the thickness of diffusive environments because of adsorbing substances redistribution on interface of dispersion phases of a various chemical nature.

Conclusion

On the basis of the carried out researches it was determined, that in the process of dispersion heterocoagulation the carry of highly dispersed system polymeric particles weight on particles of the system with the smaller dispersity is observed, as it is defined with the final distribution of particles according to their sizes. The necessity of the systems close on dispersion structure use is shown. As a result of electrokinetic properties research, the zones of dispersions' incompatibility, described by opposite marks of electrokinetic potential are established. The dependence of alkyd oligomer emulsion dispersity from its' rheological properties is established and the optimal physical-chemical and hydrodynamic conditions of steady alkyd emulsion with necessary structure production are chosen.

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