Properties of modifying additives for materials based on water polymer dispersions

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Abstract. The properties of aqueous dispersions of petroleum paraffin and ceresin, which are developed as modifying additives for water-dispersion paints and varnishes, are investigated. It has been found that such dispersions have a narrow particle size distribution. The relative coagulation rate is calculated and the rheological properties of dispersions of paraffin and ceresin are studied.

Introduction
The use of aqueous dispersions of polymers in various fields of technology necessitates their modification to meet the requirements for adhesive films formed from them. Modification of polymers makes it possible to expand their scope and improve the operational properties of products using them. To impart hydrophobicity to adhesive polymer films, control the permeability of water vapor and other gases, reduce the stickiness of products during storage, increase the protective properties, etc., natural waxes of various types (beeswax, mountain, carnauba), synthetic (Fischer-Tropsch) can be used as modifiers, polymer (polyethylene and its derivatives), solid petroleum hydrocarbons (paraffins, ceresins, microcrystalline waxes), etc. Such modifications are considered in modern periodicals and discussed at international congresses devoted to polymer composite materials and coatings [1 - 7]. Micronized waxes or aqueous wax dispersions are used to modify water dispersible materials. [6 - 8].

One of the most affordable types of waxes is solid petroleum hydrocarbons. Their films have relatively low moisture, vapor and gas permeability.

The great advantage of solid hydrocarbons is that they are pure, often white or yellowish, odorless and tasteless substances that do not contain harmful pathogenic, carcinogenic and mutagenic compounds. Solid petroleum hydrocarbons and paraffin compositions are chemically stable inert substances. 9. It is relevant to obtain their aqueous dispersions and study their properties in terms of manufacturability of using solid petroleum hydrocarbons. Aqueous dispersions of petroleum paraffin P-2 and ceresin 75 were developed in this paper [10]. The volumetric content of oil hydrocarbons in dispersions is ≈ 30%. Paraffin dispersion was stabilized using polyvinyl alcohol (PVA) with an average molecular weight (M_w) of 130,000 and an ether number of 130–150 mg KOH/g [11]. The dispersion process was carried out using a dissolver with a gear stirrer with a diameter of 40 mm and a rotational speed of 115 s⁻¹. Mixing at low speeds and dispersion was carried out at a temperature exceeding the melting point of hydrocarbons.

Experiment
It was experimentally established that the most stable dispersion of paraffin was obtained with a PVA content of 3.5% in the composition. For the dispersion under study, an analysis of variance was performed using ultramicroscopy. The particle size distribution curve is shown in...
Figure 1, from which it follows that the most probable particle size of the paraffin dispersion is 3.3 μm.

Thus, paraffin dispersions stabilized by PVA are quite stable, however, it was noted that a small amount of low-dispersed fractions floats during storage. It is known [12] that the behavior of surfactants that affects the size distribution of particles of the dispersed phase can be controlled by the introduction of hydrotropic additives into the composition of the dispersion medium. The effects of isopropyl alcohol (IPA) and propylene glycol (PG) were tested as such additives. They can effectively regulate the phase behavior of surfactants. It was found that the most stable are dispersions stabilized by PVA in combination with hydrotropic additives: 10% IPA and 4.5% PG [10].

Particle size distribution curves (Fig. 1) showed that the most probable particle size for dispersions containing, in addition to the PVA solution, IPA and propylene glycol was 3 μm. The content of coarse fractions is the smallest in the case of using IPA as a hydrotropic additive. The content of finely divided fractions with the use of IPA increases. This is most likely due to its lower dielectric constant (ε = 18.3) compared to propylene glycol (ε = 29.5 - 35.0). [13]

Studies of the aggregative stability of these dispersions were evaluated by the change in the optical density of diluted dispersions over time (Fig. 2). Using the relative change in the optical density of the dispersions, the coagulation rates of paraffin particles were calculated (Table 1).

| The composition of the stabilizing system | PVA | PVA + IPA | PVA + PG |
|------------------------------------------|-----|-----------|----------|
| Coagulation rate, hour⁻¹·10⁻³            | 14,9| 1,8       | 5,8      |

Figure 2 and Table 1 data show that the coagulation rate of paraffin dispersions stabilized by PVA in combination with propylene glycol is greater than the coagulation rate of the dispersion obtained on the basis of a solution of PVA in combination with IPA. The appearance of a maximum in the dependences is associated with preliminary enlargement of particles whose sizes correspond to the Rayleigh region, with further coagulation and flotation.
Thus, we can conclude that the best dispersion conditions for paraffin correspond to the presence of PVA and IPA in the dispersion medium. Under these conditions, a narrower particle size distribution is also achieved.

Dispersion of ceresin related to microcrystalline petroleum waxes and characterized by a significantly higher melt viscosity than paraffin is possible at the same temperatures without the use of polyvinyl alcohol, but using an ionic surfactant with a high hydrophilic-lipophilic balance (HLB). For this purpose, we used monoethanolamine oleate, for which HLB is approximately 15 [10, 14]. It was found that with a minimum oleate content of 2.8%, stable aqueous dispersions of ceresin can already be obtained. The dispersions are stable with a higher content (more than 4%) but have a high viscosity, which is caused by the viscosity of the solution of this surfactant.

The ultramicroscopy method was used to perform the analysis of variance for ceresin dispersions with different surfactant contents (Fig. 3).

**Figure 2.** Relative change in optical density of paraffin dispersions over time.

**Figure 3.** Particle size distribution of ceresin dispersions.
From the data presented in Figure 3, it can be seen that the average size of the dispersed particles is 3 μm (the same as for paraffin dispersions). Moreover, the largest proportion of particles with a size of 3 μm and the narrowest distribution curve corresponds to a dispersion containing 3.5% monoethanolamine oleate.

The results of studies of the aggregative stability of ceresin dispersions are presented in Figure 4 and Table 2.

![Figure 4. The change in optical density of ceresin dispersions.](image)

**Table 2. The coagulation rate of ceresin dispersions.**

| Monoethanolamine oleate content, % | 2.8 | 3.5 | 4.2 |
|-----------------------------------|-----|-----|-----|
| Coagulation rate, hour$^{-1}10^{-3}$ | 1.8 | 1.4 | 9.0 |

For a ceresin dispersion (Fig. 4) stabilized with 3.5% oleate, a smooth achievement of the maximum change in optical density at an exposure time of 12 days is observed. The dispersion containing 2.8% oleate reaches the maximum change in optical density after 4 days of exposure, and the dispersion containing 4.2% after 3 days.

One of the most important properties of water-dispersion materials that determine the conditions for their use are rheological properties. The results of studies of these properties are presented in Figures 5 - 7.

Figure 5 shows that the use of PG as a hydrotropic additive has practically no effect on the viscosity of the dispersion of paraffin stabilized PVA, while the use of IPA for this purpose leads to a sharp increase in viscosity at all shear rates, which is most likely associated with differences in the dispersed composition of systems.
Figure 5. Dependence of viscosity of paraffin dispersions on shear rate.

It is also seen that paraffin dispersions stabilized by PVA and PG at low shear rates have a slightly dilatant flow pattern. For dispersion containing IPA, weak pseudoplastic nature of the flow is observed.

Figure 6. Dependence of the viscosity of ceresin dispersions on shear rate (exposure time - 6 days).

Conclusion
The results of the study of the rheological properties of ceresin dispersions are presented in Figure 7, from which it follows that with an increase in the oleate content, the nature of the flow in the region of low shear rates becomes plastic, and with an increase in the shear rate, it is again Newtonian. Moreover, over time, the viscosity of the dispersions increases, due to the formation of intermolecular bonds in the surfactant solution (Fig. 4).
Figure 7. The change in viscosity of ceresin dispersions during storage:
a) the initial time, b) 2 days.

The low viscosity values of the dispersions under study at different shear rates, the pseudoplastic nature of their flow, and stability to shear deformations make them easy to use to modify polymer composite materials.

Thus, the results of studies of the fractional composition of dispersions of paraffin and ceresin, their aggregate stability, and rheological properties allow recommending them as modifying additives for materials based on aqueous dispersions of polymers for various purposes.

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