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Hydrophobisation of Water-Dispersion Paint and Varnish Material with Polysiloxane Emulsion

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Abstract

The modern market of paint and varnish materials is represented by a wide range of construction products, including those designed to protect facades of buildings and structures from atmospheric impact. Among the variety of varnishes and paints for processing and rendering decorative and protective properties to building materials, as well as from the viewpoint of environmental friendliness, the most popular products are water-dispersion paints based on acrylic dispersions. However, along with the high values of colour fastness, UV resistance and gas permeability, acrylic-based paints are insufficiently elastic and lack resistance to water. In this regard, the paper considers a method for increasing the mechanical and hydrophobic properties of acrylic paint and varnish material by introducing a hydrophobic polyethylhydrosiloxane-based emulsion containing polyethylhydrosiloxane (PEHS) – 35.20, glutaric aldehyde – 0.19, polyvinyl alcohol (PVA) – 7.75, water – 56.86 wt%, as well as by increasing the surface development (relief), achieved by increasing the volumetric concentration of pigments (VCP). The optimal range of the amounts of a hydrophobic emulsion and a coalescent into the composition of water-dispersion paints based on acrylic dispersion has been determined. To assess the stability of the coating after drying an aqueous dispersion paint modified with the aqueous polyethylhydrosiloxane emulsion, the wetting angle and free energy of the surface were evaluated using two liquids of different polarities, namely distilled water and diiodomethane. The possibility of modifying the aqueous dispersion paint, characterised by VCP of 70–80 %, by the polyethylhydrosiloxane hydrophobic aqueous emulsion in the amount of 5–5.5 %, combined with ethylene glycol (4.5–5.5 %) has been established, which makes it possible to obtain a hydrophobic coating with a wetting angle of up to 100°. By comparing the wetting angle values of the coatings, it has been shown that in the absence of the hydrophobic additive, this parameter is lower by 12.5 % than the parameter of the modified sample.

Keywords: hydrophobisation, polyethylhydrosiloxane emulsion, water dispersion paints, wetting angle, surface energy

INTRODUCTION

Paint and varnish industry annually fills the market with products exhibiting diverse decorative effects and serving as coating layers for various kinds of construction materials. However, paint and varnish materials need modification and improvement of their quality due to the influence of climatic conditions and aggressive environment [1–5].

In the previous studies [6], a method was proposed to prepare an aqueous emulsion of polyethylhydrosiloxane (PEHS) GKZh-94 on the basis of polyvinyl alcohol modified with glutaric aldehyde.

Distinctive features of this emulsion are its coagulability during drying under the action of a coalescent (an additive to decrease the temperature of film formation) and high hydrophobic efficiency on the developed surfaces of such materials as fine-grained concrete and fibrous concrete [7]. However, the coating formed by this emulsion is unstable against mechanical action.

Water-dispersion paint (WDP) for walls and ceilings was chosen as the basis possessing sufficient mechanical and decorative-protective characteristics. Water-dispersion paints based on acrylic dispersions are most universally applicable: they are stable against layering, possess high pigment capacity, are easy to apply and fast-setting. Coatings based on them well conserve the colour, endure intense ultraviolet radiation, possess high moisture and gas permeability, good adhesion to various surfaces, are stable against mechanical action, but exhibit sufficient elasticity [8].

The goal of the present work is development of a composition for acrylic WDP by modifying it with a hydrophobic emulsion based on polyethylhydrosiloxane, and investigation of the properties of modified coatings.

EXPERIMENTAL

Acrylic dispersion A-128 was used as the base to make WDP composition with different volume concentrations of pigments (VCP) to paint vertical surfaces. Specific features of paint application on vertical surfaces are prevention of pain runs in the case if thick coatings are applied, and limited spreading for concealing the mechanical action of a brush and roller with their characteristic small shear rates.

The composition of pigment paste is: talc, calcite, and rutile. The dynamic viscosity of the pigment paste with VCP 75 % was 0.49 Pa · s. Measurement was carried out with the help of a rotating viscometer Rheotest RN4.11 (Germany) using a cylindrical system Searle.

The hydrophobic emulsion for WDP modification comprises the dispersed phase (PEHS) – 35.20 wt%; dispersing medium (water) – 56.86 wt%; emulsifier of the dispersed phase (PVA) – 7.75 wt%; modifier PVA and WDP acetalation agent (glutaric aldehyde) – 0.19 wt%.

On the basis of previous investigation proving the efficiency of ethylene glycol with respect to the angle of polymer coating wetting [9], ethylene glycol in the concentration of 2, 5 and 8 % of WDP mass (without taking emulsion into account) was introduced into the emulsion to improve selective coalescence of PEHS.

A paint-and-varnish coating is usually formed by applying the pain onto fine-grained concrete, facing plaster or plastic filler (laying thickness >0.3 mm), which results in smoothing down the developed relief of mineral surface. However, to provide a comparative assessment of the effect of VCP and PEHS emulsion on the wetting angle, smooth glass substrates were chosen as model surfaces for the deposition of WDP compositions.

Thus, the wetting angle and the free surface energy (FSE) were assessed using a smooth substrate made of colourless plate glass. The sample for investigation was WDP modified with the hydrophobic emulsion and kept at room temperature for 7 days till complete drying and obtaining a paint-and-varnish film according to GOST 19007-73 “Paint and varnish materials. Method to determine time and extent of drying”. The wetting angle was measured using the sessile drop method with the help of DSA 30 analyser (KRÜSS GmbH, Germany) and ADVANCED software. The free surface energy is a sum of the polar and dispersive components, and it is determined by the Owens, Wendt, Rabel and Kaelble (OWRK) method from the linear regression plotted on the basis of wetting angle values determined using the liquids with known polar and dispersion components – distilled water and diiodomethane.

The SigmaPlot software was used for the visual demonstration of results.

RESULTS AND DISCUSSION

The compositions of WDP with the constant value of dry residue 65 %, with acrylic dispersion content 32 %, with different VCP concentrations –50, 60, 70 and 80 %, and with the addition of hydrophobic emulsion in the amount of 3, 6 and 9 % of WDP mass were prepared (Fig. 1). The total number of samples was 16. The data obtained in the investigation were approximated by the quadratic regression equation with the confidence coefficient $R^2 = 0.96$:

$$\theta_K = 154.04C_{VCP} - 57.06C_E - 108.99C_{VCP}^2 - \\ - 620.54C_E^2 - 602.76C_{VCP}C_E \quad (1)$$

where θ_K is the contact angle, deg; C_{VCP} is the volume concentration of pigments, vol%; C_E is the concentration of hydrophobic emulsion, wt%.

An increase in the amount of hydrophobic emulsion added causes an almost linear increase in the wetting angle from 50 to 65° at small VCP values (<50 %). A higher degree of wetting angle increase with the addition of the emulsion is demonstrated by the compositions with VCP >80 %. This may be due both to the better interaction of PEHS with the mineral particles of pigments and fillers, and to the better developed surface structure of coatings with decreased acrylic film-former content. The effect of the surface itself can be indirectly assessed from the parabolic dependence of the wetting angle on VCP in the absence of hydrophobic emulsion. Here, the peak wetting angle equal to 55° at VCP = 70 % can be observed, decreasing with further increase in VCP. This can be explained by the hydrophilic capacity of the mineral part of WDP that contributes into the synergistic effect in the interaction with PEHS during the formation of a paint-and-varnish coating from the acrylic WDP volume-modified by polyethylhydrosiloxane emulsion on a porous-capillary construction material. However, this result still cannot be considered being positive, because the required hydrophobisation of the coating with wetting angle >90° is achieved only at high VCP (>80 %), which obviously causes a decrease in the durability of these coatings.

To achieve comprehensive understanding of the wetting mechanism for the coatings formed from the WDP compositions under investigation, the tests on wetting angle determination were carried out using diiodomethane. The results of tests are shown in Fig. 2. Similarly to (1), the data were approximated by the quadratic regression equation with confidence coefficient $R^2 = 0.98$:

$$\theta_K = 185.6C_{VCP} + 163.1C_E - 157.7C_{VCP}^2 - 4361.8C_E^2 + 732.7C_{VCP}C_E \quad (2)$$

The mode of WDP coating wetting with diiodomethane generally follows the pattern of wetting with water, except for absolute values. Thus, the coatings failed to achieve oleophobicity even with high VCP level and large amount of the emulsion introduced. A critical kink is seen on the curves at lower concentrations of the hydrophobic agent (6–8 %) and VCP (70–80 %) in comparison with the sole extremum on the diagram of wetting with water (see Fig. 1 and 2). This discrepancy can be theoretically explained by the increasing surface roughness and related surface area. The mechanism of wetting angle changes on a rough surface is described by the Ventsel-Deryagin equation:

$$\cos \theta_r = R_\Delta \cos \theta_{sm} \quad (3)$$

where R_Δ is the ratio of actual surface to its projection on the plane; θ_{sm} and θ_r are wetting angles for the smooth and rough surfaces, respectively, deg.

It follows from equation (3) that for the wetting angle <90° the growing surface should cause a decrease in angle cosine ($\cos \theta_r$) in direct proportion to the increasing wetting area. Thus, the roughness can explain the above-described critical kink on the plots for diiodomethane, however, the absence of such a kink on the water-wetting

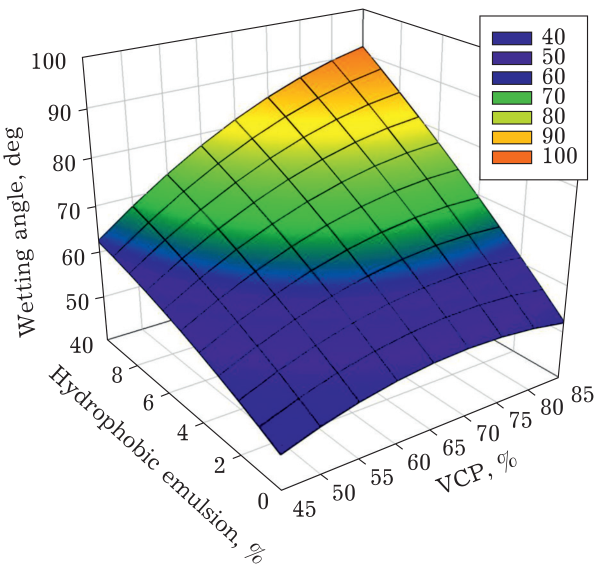

Fig. 1. Dependence of the water-wetting angle on the WDP coating with different VCP level and the amount of hydrophobic emulsion added. Here and in Fig. 2–4: WDP is water-dispersion paint, VCP is the volume concentration of pigments.

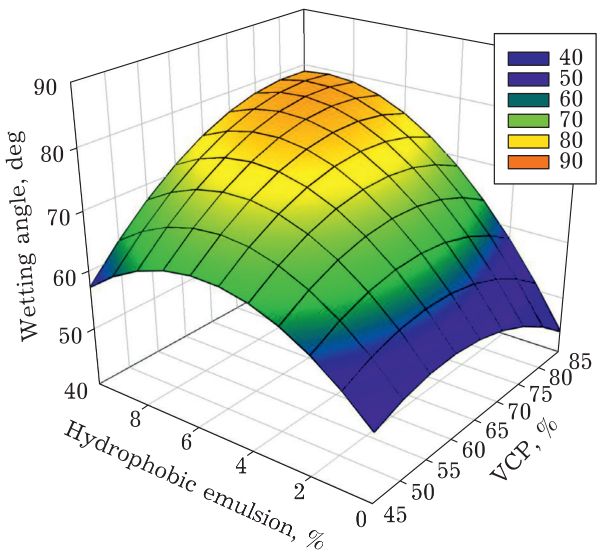

Fig. 2. Dependence of diiodomethane-wetting angle on WDP coating with different VCP levels and amounts of the hydrophobic emulsion added. For designations, see Fig. 1.

diagram for the surface of WDP samples with hydrophobic emulsion remains unclear (see Fig. 1).

To solve this problem, we plotted the diagrams of the dependences of FSE, its polar and dispersion components on VCP value and the amount of the introduced emulsion relying on the obtained values of wetting angle for the coating formed from WDP with hydrophobic emulsion added. The data are presented in Fig. 3.

The polar component of FSE demonstrates an almost linear decrease with an increase in the amount of hydrophobic emulsion introduced into WDP. A slight increase in FSE occurs with a decrease in VCP, nd the change is much more intense with an increase in the amount of the emulsion introduced. This may be related to the continuity of the coating and the emergence of pigments and fillers on the surface of mineral particles. Quite contrary, the value of dispersion component only weakly correlates with VCP level, however, it decreases sharply with an increase in the amount of emulsion to 5 %. For emulsion concentration 6 to 10 %, no substantial changes in the energy of dispersive interaction occur. This coincides with the position of the critical kink on the plot showing the dependence of the angle of wetting with diiodomethane on WDP composition (see Fig. 2), which is explained by a decrease in Van ser Waals energy.

The above-described behaviour of the polar component of FSE can be explained by non-uniformity, involvement of air, and the layering ability of the mixture of acrylic dispersion with the hydrophobic emulsion. The main method to eliminate this phenomenon is to introduce coalescents into WDP composition. The reasonable choice of coalescents allows us to improve the interaction of emulsion drops with the particles of acrylic dispersion.

The best coalescents for acrylic dispersions are the ethers of polyhydric alcohols, such as ethyl cellosolve, butyl cellosolve, texanol, etc. However, in the case of their high concentrations in WDP, these coalescents can cause an increase in the hydrophobic characteristics of the coatings [10–12]. The positive effect of ethylene glycol as a coalescent for the emulsions based on PEHS has been confirmed previously [9]. So, ethylene glycol will be eminently suitable for the selective coalescence of PEHS under a weak action on acrylic film-forming agent. So, in the present work, we have investigated the effect of the amount of ethylene glycol on the hydrophobic ability of the emulsion based on PEHS, prepared by the direct reagents mixing.

The result shown in the diagram (Fig. 4) demonstrates the change of the hydrophobic ability of the paint-and-varnish coating caused by the

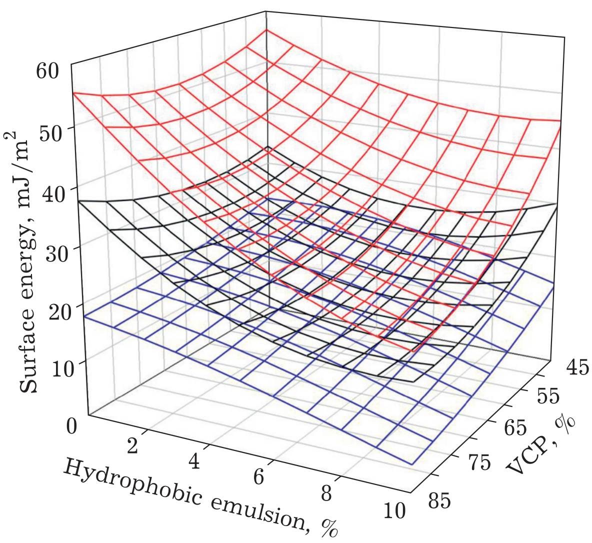

Fig. 3. Dependence of the free surface energy (FSE), its polar and dispersive components for the WDP coating with different VCP levels and amounts of hydrophobic emulsion added. For designations, see Fig. 1.

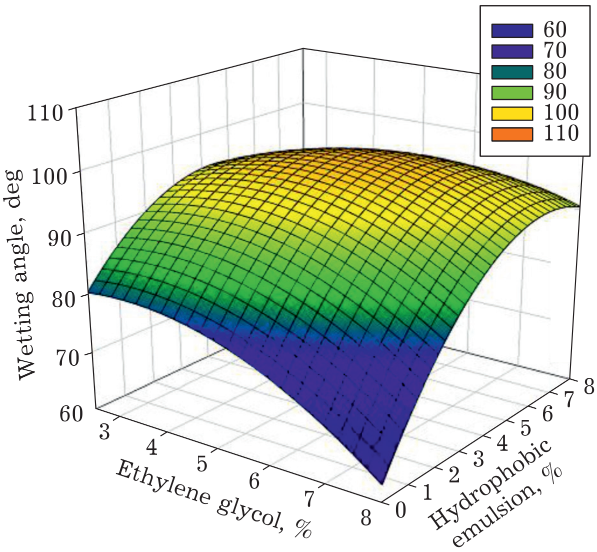

Fig. 4. Changes of the wetting angle depending on the amount of hydrophobic emulsion and ethylene glycol introduced into WDP. For designations, see Fig. 1.

introduction of ethylene glycol into WDP. It has been established that without the hydrophobic emulsion, with ethylene glycol introduced into WDP in the amount of 4.5 % and more, the wetting angle starts to drop sharply by 25 % due to the increasing liophilicity of the coating. However, for initial ethylene glycol content of 3 wt% in WDP, and with the introduction of the emulsion in the amount of 4 wt%, the wetting angle of this coating becomes >90° within the whole range of ethylene glycol concentrations, that is, an increase by 12.5 % is observed. It should be specially stressed that the ratio of the hydrophobic emulsion to ethylene glycol is approximately 1 : 1 with the hydrophobic mode of surface wetting, which is essentially different from the case of the emulsion itself applied on the glass surface, when the optimal ratio was 10 : 1 (the ratio of the emulsion to ethylene glycol is based on the results of the evaluation of the possibility to increase the wetting angle of polysiloxane emulsions by introducing polyalcohols, as described in a previous publication of the authors of the present article [9]).

The reasonable concentration of the emulsion introduced into WDP is 5–5.5 % with ethylene glycol content 4.5–5.5 % in WDP. This composition provides the wetting angle equal to 99.4°. The hydrophilic surface formed by the reference WDP composition is characterised by a not very large wetting angle (80°). The introduction of emulsion with ethylene glycol as the functional additive to WDP in low concentrations (5–5.5 %) is sufficient to reach wetting angle values characteristic of hydrophobic surfaces. So, the formation of hydrophobic coating with similar wetting angle parameters to those for a clean hydrophobic emulsion coating on glass. A decrease in wetting angle values for the surface formed by WDP with the addition of hydrophobic emulsion in the amount of 5–5.5 %, together with the coalescent component – ethylene glycol (4.5–5.5 wt%), in comparison with wetting angle values for the surface formed by modified WDP without ethylene glycol, is not over 5 %.

CONCLUSION

As a result of the studies, the method is proposed to use the hydrophobic emulsion as an additive into acrylic water-dispersion paint. The introduction of the hydrophobic emulsion within the concentration range of 5–5.5 wt% together with the coalescent component, ethylene glycol (4.5–5.5 wt%), into the water-dispersion paint with VCP 70–80 wt% allows obtaining the hydrophobic coating with a wetting angle up to 100°, comparable with the wetting angle for the case when the coating is composed of pure aqueous polyhydrosiloxane emulsion, but with lower emulsion consumption. Thus, an increase in the wetting angle value by 12.5 % in comparison with the reference hydrophilic coating composed of the water-dispersion acrylic paint is achieved.

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