Effect of mineral fillers on the wetting of water-based polymer dispersions

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Abstract. To ensure reliable protection of porous plastered facades, water-based polymer dispersions must meet a set of properties for moisture absorption and vapour permeability. One of the most significant indicators in assessing moisture absorption is the hydrophobic properties of the coating, which characterizes their water repellency. Therefore, the article studied the effect of the dispersed mineral fillers content based on silicates and aluminosilicates on the wetting of water-based polymer dispersions and determined the possibility of their use as decorative and protective materials for plastered building facades finishing. It was found that the studied samples of water-based polymer dispersions can be used as facade coatings with high vapour permeability and low moisture absorption, which is confirmed by studies of the contact angle. The optimum values along the contact angle verge towards the hydrophobic coatings.

1. Introduction

Water-based polymer dispersions are becoming more widespread as protective and decorative coatings of building facades due to the absence of toxic organic solvents, decorative properties, high processability and other advantages compared to organic solvent-based coatings [1-3].

To ensure reliable protection of porous plastered facades, water-based polymer dispersions must meet a set of properties for moisture absorption and vapour permeability. Sufficient vapour permeability to eliminate the difference in the partial pressure of water vapour between the base material and the outer layer eliminates the formation of condensate, prevents the plaster peeling and freezing of the walls indoors. Low moisture absorption of the coating prevents the penetration of water into the substrate. But, on the other hand, a certain permeability of the coating for water vapour guarantees faster drying. One of the most significant indicators in assessing moisture absorption is the hydrophobic properties of the coating, which characterizes their water-repellency [4].

The hydrophobic properties are characterized by the value of the contact angle of the coating with water, and the higher it is, the higher are the hydrophobic properties of the coatings. It is proved that the value of the contact angle with water up to 90° indicates the wettability of the coating, and above 90° – indicates its water-repellency.

The purpose of the work is to study the influence of the content and nature of dispersed mineral fillers based on silicates and aluminosilicates on the wetting of water-based polymer dispersions (WB-PD) and the possibility of their use as decorative and protective materials for plastered building facades finishing.
2. Materials and methods

Styrene-acrylic dispersion of ACRONAL® 290 D, produced by BASF (non-volatile compounds content – 50 % wt, pH 7.5-9.0, average particle size about 100 nm, viscosity at 23 °C (ISO 3219, DIN 53019) at shear rate – 100 s⁻¹, 7-15 mPa·s) was used as a paste film thickness.

Cellulose acrylic thickeners, polymer-based mineral oil free antifoam, a dispersant, coalescent agent based on a mixture of ether and alcohol, and a preservative additive were used as dispersion modifiers.

Hollow aluminosilicate microspheres and silicates based on hydrophobic AEROSIL® A-1/300 were used as mineral fillers [5-9].

Hollow microspheres (MS) are finely dispersed, free-flowing powders consisting of spherical thin-walled aluminosilicate particles with a diameter of 10-100 μm and a specific surface of 0.61 m²/g.

In order to regulate the rheological properties of WB-PD, the hydrophobic AEROSIL® AM-1/300 (AEROSIL®) filler was used, which also serves as a stabilizer for water-based polymer dispersions, prevents the pigment sedimentation and attributes thixotropic properties. Hydrophobic AEROSIL® is highly dispersed amorphous silicon dioxide with a hydrophobic surface of the particles obtained by treating the surface of the particles with anchors that replace the silanol groups contained on the surface of the particles with non-polar organic groups such as methyl, with a specific surface of 200 m²/g and an average density of 0.051-0.059 g/cm³.

To determine the wetting angle (Θ), the Sessile drop method was used [10]. The essence of the method lies in the fact that a drop of water was placed using a capillary at a temperature of 20 ± 1 °C on a hard even surface of WB-PD, which was studied, and a drop of water was placed using a capillary and the height (h) and width of the drop base (d) were measured. Determination of contact angle of the coatings was carried out on a Double-Coordinate Measuring Machine DIP-6U with a goniometric device. The measurements were carried out in transmitted light; the accuracy of measuring the contact angles was ± 2°. The calculation of the contact angle was carried out according to the formula (1) for a spherical head at Θ <90°:

\[
\cos \Theta = \left(\frac{(d/2)^2 - h^2}{(d/2)^2 + h^2}\right)
\]

Determination of vapour permeability was carried out according to EN ISO 7783 using the dry cup method. The vapour permeability \( V \), (g/m²·day) and the diffusion ability with respect to water vapour \( S_d \), (m) were calculated by changing the mass of the cup and the area of the test surface [11, 12].

To assess moisture absorption (according to DSTU EN 1062), by immersing samples in water at 23 °C, concrete slab samples were used, on one side of which the studied WB-PD were applied. The moisture absorption was determined by the change in mass and the W-indicator was calculated, kg/(m²·hour⁰.⁵).

According to the theory of facade protection according to Künzel [13, 14] to ensure the structural physical equilibrium of the facade for coatings, the following condition must be fulfilled (2):

\[
W \cdot S_d \leq 0.1, \quad (kg / m² \cdot hour^{0.5})
\]

3. Experimental

A coating based on unfilled styrene-acrylic water-dispersion polymer is characterized by a contact angle of 44°. The value of the indicator is due to the chemical composition and surface properties of the fillers, their hydrophilicity, chemical composition and degree of filling.

Data on the effect of dispersed mineral fillers on the contact angle of modified WB-PD are shown in Table 1.

As a result of the studies, it was found that in the case of the introduction of one filler, the contact angle increases with increasing filler content to a certain limit, after which there is a decrease in the contact angle when reaching the maximum filling (Table 1).
Table 1. Dependence of the contact angle of WB-PD on the dispersed mineral fillers content.

| Filler, weight % | Contact angle $\Theta$,° | Filler, weight % | Contact angle $\Theta$,° |
|------------------|--------------------------|------------------|--------------------------|
| AEROSIL®         |                          | Microspheres     |                          |
| 0.5              | 48                       | 10               | 53                       |
| 1.0              | 57                       | 20               | 63                       |
| 1.5              | 60                       | 30               | 72                       |
| 2.0              | 61                       | 40               | 65                       |

With the introduction of AEROSIL® silicate filler in an amount of 0.5 to 2 wt.%, an increase in the contact angle by 4-16° is observed, respectively, which is associated with a decrease in the number of active centers on the coating surface due to the interaction between the active centers of the styrene-acrylic dispersion and filler.

The contact angle of styrene-acrylic dispersion depending on the aluminosilicate filler MS content also tends to increase with increasing filler content from 10 to 30 wt.% by 9-25°, respectively. However, when the filling content exceeds 30 wt.%, an inflection point is observed, followed by a decrease in the contact angle by 7° at the point of 40 wt.%, which is apparently associated with the achievement of the maximum volumetric concentration of the filler, as a result of which the wetting of the filler with a binder deteriorates, which leads to the formation of a defective coating structure.

To justify the practical application of the developed WB-PD as protective and decorative coatings of facades, the contact angle and pair correlation of the building-physical properties of these coatings in the coordinates of the Künzel diagram were evaluated.

The dependence of the contact angle and the criterion of structural physical equilibrium on the combined effect of silicate AEROSIL® mineral fillers and dispersed aluminosilicate MS was evaluated using the response surface (Figure 1).

The main response functions were the contact angle $y_1$ (3) and the criterion of structural physical equilibrium $y_2$ (4). The obtained regression equations have the form of:

$$y_1 = 76.89 + 0.67x_1 + 2.67x_2 + 0.33x_1^2 - 10.67x_2^2 - 1.25x_1x_2$$

$$y_2 = 0.009 - 0.002x_1 - 0.003x_2 - 0.001x_1^2 - 0.003x_2^2 - 0.002x_1x_2$$

An analysis of the regression equations (3) and response surfaces of the dependence of the WB-PD contact angle of contact on the content of MS ($x_2$) AEROSIL® ($x_1$) (Figure 1, a) clearly shows that when using these fillers, the dependence is not linear. In this case, the contact angle substantially depends on the MS content, and the introduction of AEROSIL® does not significantly increase this...
indicator. The maximum value of $\Theta = 79^\circ$ is achieved with the introduction of 30 wt.% MS and 1.0 wt.% AEROSIL®, and the minimum $\Theta = 62^\circ$ – with MS 10 wt.% and 0.5 wt.% AEROSIL®.

The dependence of the criterion of structural and physical equilibrium (4) of the WB-PD facade depending on the concentration of AEROSIL® ($x_1$) and MS ($x_2$) primarily depends on the content of MS, and the optimum point is observed when the joint content of MS 40 wt.% and AEROSIL® 1.5 mass. %. All the studied WB-PD samples correspond to the criterion of structural physical equilibrium of the facade $W \cdot S_d \leq 0.1$, ($kg \cdot m^2 \cdot hour^{-0.5}$).

4. Conclusions
As a result of studies on the effect of dispersed mineral fillers on the contact angle and vapour permeability of water-based polymer dispersions, it was found that all the WB-PD samples studied can be used as facade coatings with high vapour permeability and low moisture absorption, which is confirmed by the studies of contact angle. The optimum values along the contact angle approach the coatings with the hydrophobic nature of the surface ($\Theta = 80^\circ$) and the Künzel condition for the structural physical equilibrium of the facade is fulfilled when $W \cdot S_d \leq 0.1$, ($kg \cdot m^2 \cdot hour^{-0.5}$).

The data obtained allow us to optimize the composition of WB-PD for external protection of plastered facades in order to obtain coatings with high water repellent ability and a sufficient level of vapour permeability. This protects the external surfaces of building concrete structures from the influence of atmospheric factors and the formation of condensation on the internal surfaces, reduces the internal freezing of walls, which prevents plaster peeling.

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