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Research of the Influence of Silicate Fillers on Water Absorption and Microstructure of Styrene-Acrylic Dispersion Coatings

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Abstract. Permeability is important to ensure the protective properties of coatings based on styrene-acrylic dispersions. This indicator characterizes the complex of insulating properties of coatings, their ability to prevent the penetration of liquids, vapors and gases from the environment to the surface to be protected. It was studied the effect of aluminosilicate microspheres, which are characterized by the hydrophilic nature of the surface and highly dispersed silicate filler aerosil with a hydrophobised surface on the water absorption of styrene-acrylic coatings. Decreased of water absorption of styrene-acrylic coatings filled with aluminosilicate microspheres with the introduction of hydrophobised aerosil is linked to the fact that the fine aerosil with a high specific surface area provides the formation of a more densely packed structure. Thus, partially filling the interspherical space, which is formed by particles of microspheres with a diameter of 10-100 μm and reduces the surface defect of the styrene-acrylic coating. Localization on the surface of defective structures of particles of hydrophobised aerosil leads to a decrease in wetting of defective structures with water. Resulting deteriorating wetting the surface of the styrene-acrylic coating. Micrographs were taken to assess the nature of the distribution of aerosil on the surface of the styrene-acrylic coating. The analysis of the obtained micrographs confirms that the introduction of microspheres form large agglomerates, between which there are vacancies, which will negatively affect the technological and operational properties of the developed coatings. At the same time, the introduction of aerosil allows to obtain a more orderly structure, which allows to obtain a coating with lower internal stresses, increased aggregate stability and, as a consequence, with improved technological and operational properties.

Introduction

Permeability is essential for the protective properties of styrene-acrylic dispersion coatings. It characterizes the complex of insulating properties of coatings, their ability to prevent the penetration of liquids, vapors and gases from the environment to the protected surface.

Permeability is an indicator that is determined by the properties of the composition of the film material and the environmen [1, 2, 3, 4, 5]. Most often have to face with water vapor and water - permeability in practice.

Penetration of water vapor and water through thin-layer paint coatings to the substrate carried out as a result of capillary flow and diffusion. Capillary flow has coatings with mechanical porosity, that is, with capillaries, pores, microcracks.

The porosity of the coating is distinguished between explicit and latent. The first is associated with the presence of open pores; it is easily detected by conventional continuity measurement methods. Latent porosity due to closed pores - these are weak defects in the film, which usually quickly appear during the operation of the coating.

The penetration of a substance through the film consists of sorption (dissolution), diffusion and desorption from the other side of the film according to modern concepts. This is equally true when gases, vapors, low-molecular-weight liquids and water penetrate through the film.

With the absence of a strong interaction between the sorbent and the sorbate, the sorption equilibrium is established quickly and the rate of the total process is mainly determined by the rate of the diffusion process described by the Fick equation (1):

$$Q = -D\frac{dC}{dx}S\tau, \qquad (1)$$

where Q – the amount of substance that diffused; D – the diffusion coefficient; $\Delta C/\Delta x$ – concentration gradient; S – area; τ – time.

In non-polar and weakly polar polymers, the solubility of polar liquids (water, electrolytes) and gases is low and their sorption obeys Henry's law (2) associates the concentration of a solute with a pressure drop:

$$-\frac{dC}{dx} = \sigma\frac{dP}{dx}, \qquad (2)$$

where P – the permeability coefficient, σ – the sorption coefficient.

At contact of polar polymers with polar substances sorption processes are complicated: the concentration of the sorbed substance increases disproportionately to the pressure drop, as follows from Henry's law. Due to the interaction of polar groups, absorption often reaches a large value; the diffusion and permeability of the coatings increase accordingly.

Therefore, it was of interest to research the effect of silicate fillers on water absorption and microstructures of coatings based on styrene-acrylic dispersion.

Materials and Methods

Styrene-acrylic dispersion (non-volatile compounds content – 50 wt, pH 7.5-9.0, average particle size of about 100 nm, viscosity at 23 °C (ISO 3219, DIN 53019) was chosen as a binder. Dispersion modifiers used cellulose and acrylic thickeners, antifoam, dispersant, coalescent based on a mixture of ether and alcohol and preservative additive [6, 7, 8, 9].

Hollow aluminosilicate microspheres (MS) and silicates based on hydrophobised aerosil (grade A-1/300) were used as silicate fillers.

Hollow microspheres are finely divided, free-flowing powders consisting of thin-walled spherical aluminosilicate particles with a diameter of 10-100 μm and a specific surface area of 0.61 m^2/g. The microspheres can be evacuated and filled with rarefied air (depending on the conditions of their production) and, due to the successful combination of spherical shape, controlled dimensions, low density, high compression strength, heat and sound insulation and dielectric properties, are one of the promising man-made fillers to obtain heat-insulating coatings based on aqueous dispersion of polymers [10, 11, 12].

To control the rheological properties, a hydrophobised aerosil filler (specific surface area of 200 m^2/g and average density of 0.051-0.059 g/cm^3) was used, which also acts as a stabilizer for aqueous polymer dispersion, gives thixotropic and water-repellent properties. aerosil colloidal particles have a large supply of surface energy and easily form reversible mesh coagulation structures [13, 14, 15].

Morphological analysis of the surface of styrene-acrylic coatings was carried out to analyze the effect of silicate fillers on water absorption and water diffusion processes [16, 17, 18].

The morphology of the coatings was researched from the testers of the raster electronic microscope TescanVega 3 LMH in the modes of secondary and reversible electrical distribution at an accelerating voltage of 30 kV.

The samples were coated with a thin (about 10-20 nm thick) layer of chromium immediately before being placed in an electron microscope chamber to provide the electrical conductivity required for performing SEM studies. Chromium was applied by thermal vacuum evaporation in a SELMA VUP-5 vacuum chamber at a residual gas pressure of 10-5 Torr.

Discussion

It was studied the effect of aluminosilicate microspheres, which are characterized by the hydrophilic nature of the surface and highly dispersed silicate filler aerosil (grade A-1/300) with a hydrophobised surface on the water absorption of styrene-acrylic dispersion coatings.

The method consists in determining the mass of water (Δm, %), absorbed by loose film immersed in water at a temperature of 23 °C and a test time of 28 days.

Figure 1, a demonstrates the dependence of the influence of the quantitative content of aerosil (0.5; 1.0; 1.5 wt.%) and aluminosilicate microspheres (20; 30; 40 wt.%) (Fig. 1, b) on the water absorption of the compositions based on styrene-acrylic dispersion (SAD).

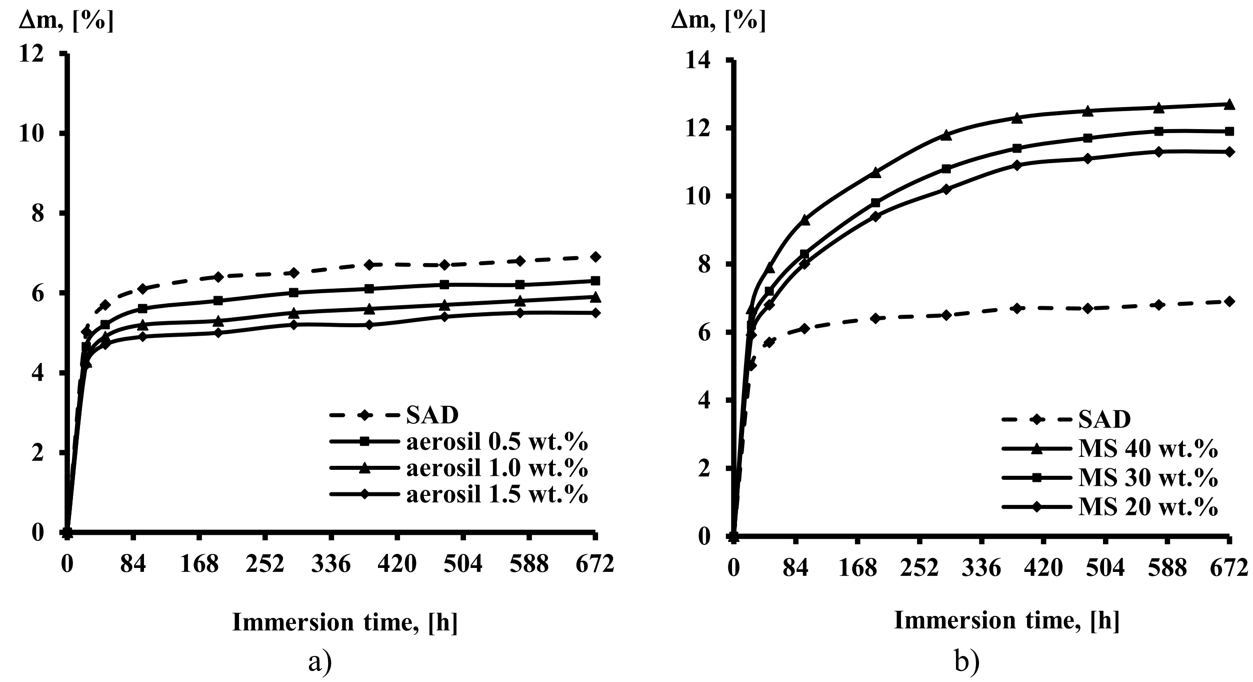


Fig. 1. Change in water absorption of SAD in depending on the content of aerosil (a) and aluminosilicate microspheres (b)

The presented dependences (Fig. 1, a) are shown that the introduction of hydrophobised aerosil (0.5, 1.0, and 1.5 wt.%) makes it possible to reduce the water absorption of the studied SAD films by 9, 15 and 19 %, respectively.

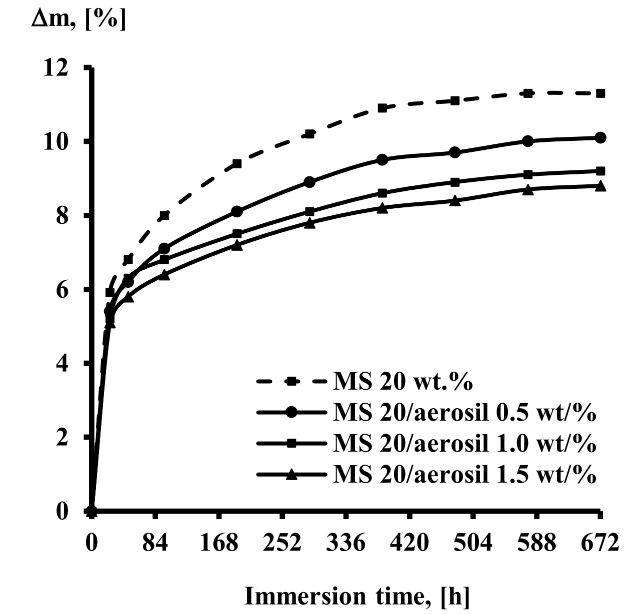
This is probably due to the filling with particles of hydrophobised aerosil, which has a high specific surface area of contact with styrene-acrylic dispersion, free vacancies in the volume of the film that has formed, and the formation of a boundary layer with hydrophobised aerosil on the surface of the styrene-acrylic film. This leads to decrease in the defect of the surface structure and as consequence reduces the diffusion and sorption of water of the studied samples SAD.

Analysis of the obtained dependences (Fig. 1, b) shows that the introduction of aluminosilicate microspheres (20, 30, and 40 wt.%), which are thin-walled spherical particles with a diameter of 10-100 microns, leads to an increase in water absorption by 66, 75 and 85 %, respectively.

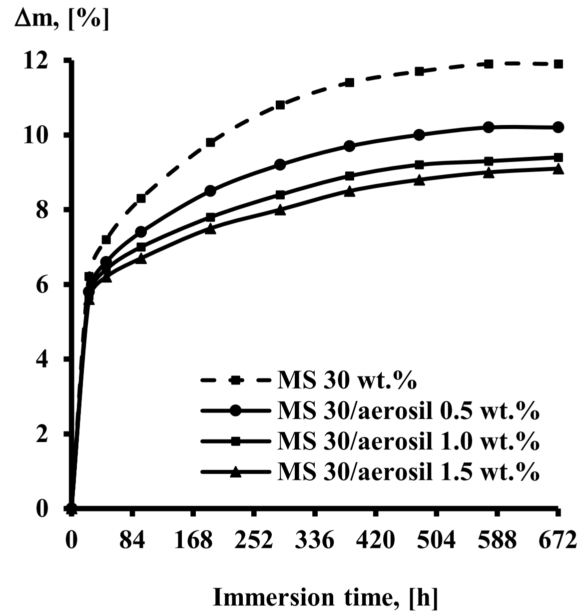
This is due to the poor contact of aluminosilicate microspheres with the styrene-acrylic dispersion, as well as the difficulty of their uniform distribution throughout the entire volume of the dispersion and the presence of voids between the contacting spherical particles.

As a result, the amount of free vacancies in the bulk of the film increases, which leads to the formation of structural defects and pores on its surface.

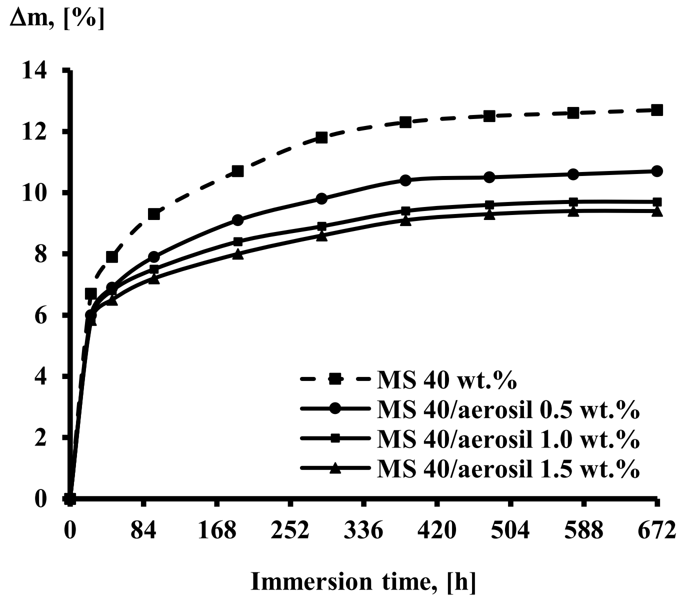
The effect of the combined introduction of aluminosilicate microspheres and hydrophobised aerosil on the water absorption of studied films SAD are shown in Fig. 2.



a)



b)



c)

Fig. 2. Change in water absorption of SAD filled with microspheres 20 wt.% (a), 30 wt.% (b) and 40 wt.% (c) depending on the aerosil content

Decreased of water absorption of styrene-acrylic coatings filled with aluminosilicate microspheres with the introduction of hydrophobised aerosil is linked to the fact that the fine aerosil with a high specific surface area provides the formation of a more densely packed structure. Thus, partially filling the interspherical space, which is formed by particles of microspheres with a diameter of 10-100 µm and reduces the surface defect of the styrene-acrylic coating. Localization on the surface of defective structures of particles of hydrophobised aerosil leads to decrease in wetting of defective structures with water, as a result deterioration of the wetting of the styrene-acrylic coating surface and capillary diffusion decreases.

It should also be noted that an increase of aerosil content from 1.0 to 1.5 wt.% doesn't have significant effect on the water absorption rate, especially for compositions containing 30, 40 wt.% MS (increase in Δm to 1%).

This is probably due to the achievement of the limiting concentration of fillers for the formation of a dense packed structure of a polymer styrene-acrylic film and the filling of available free vacancies with particles of hydrophobised aerosil.

An indirect indicator of the adsorption interaction at the SAD phase interface is the diffusion of liquid media. According to the experimental data on water absorption, the diffusion coefficients of SAD were calculated depending on the degree of filling of aerosil and aluminosilicate microspheres in accordance with the method proposed in the work [19]. The data are presented in Table. 1 and Fig. 3.

Table 1. Diffusion coefficient of distilled water of films based on SAD filled with aerosils and microspheres

Compositions, [wt. %]	Diffusion coefficient, $D \cdot 10^{+8}$ [cm^2/s]
SAD	1.97
SAD / 0.5 aerosil	1.55
SAD / 1.0 aerosil	1.41
SAD / 1.5 aerosil	1.36
SAD / 20 MS	6.51
SAD / 30 MS	7.32
SAD / 40 MS	8.44

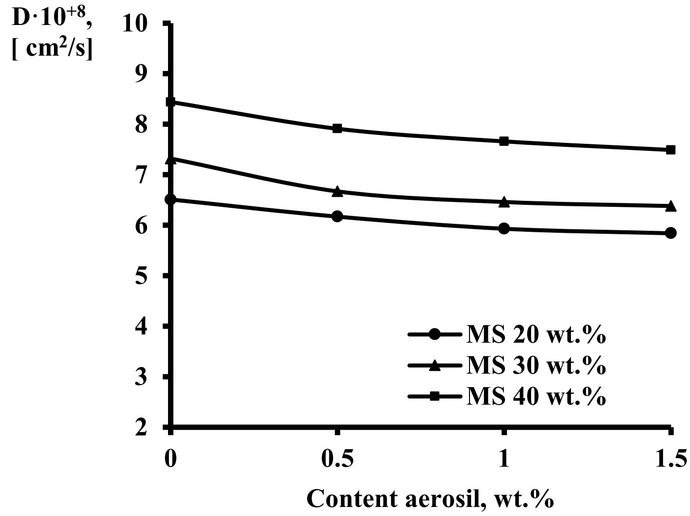


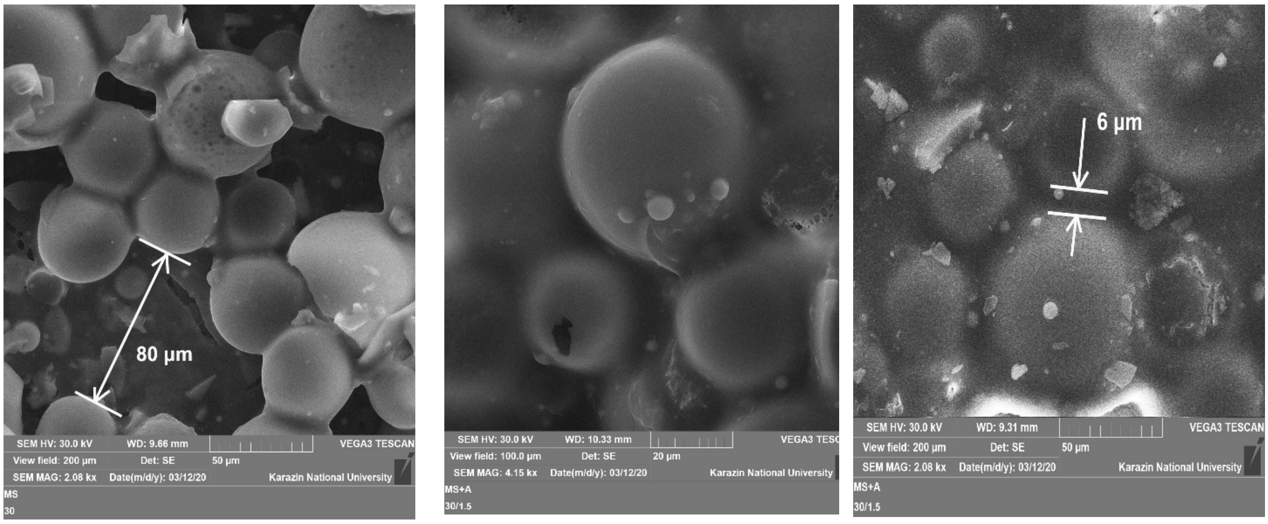
Fig. 3. Diffusion coefficient change of distilled water of SAD films filled with MS (20, 30, 40 wt.%) from the content of aerosil (0.5; 1.0; 1.5 wt.%)

Table 1 and Fig. 3 demonstrate that the introduction the introduction of MS increases the diffusion of water into the SAD paint coating by 3-4 times.

The introduction of aerosil leads to a decrease in water diffusion by 20-30%, which confirms the advisability of introducing small aerosil additives into SAD filled with aluminosilicate microspheres.

Morphological analysis of the surface of styrene-acrylic coatings was carried out to analyze the effect of the content of silicate fillers on water absorption and water diffusion processes.

The distribution of fillers in the styrene-acrylic dispersion are shown in micrographs of the surface (Fig. 4).



a) b) c)

Fig.4. Micrographs of the surface of SAD filled with 30 wt.% MS (a) and aerosil 1.5 wt.% (b, c)

The analysis of the obtained micrographs confirms that MS form large agglomerates (Fig. 4, a), between which there are free vacancies (30-80 μm), which negatively affects the operational properties of the developed coatings.

At the same time, the introduction of aerosil allows to obtain more ordered structure: layer of smaller particles of MS is formed in a circle of large particles of MS and free vacancies are filled with aerosil particles (3-8 μm) (Fig. 4 (b, c)). This allows to obtain a coating with lower internal stresses, increased aggregate stability and, as a consequence, with improved technological and operational properties.

Conclusions

It has been established that the introduction of small additives of hydrophobised aerosil into the styrene-acrylic dispersion leads to a decrease in the water absorption of coatings by 11-25% and water diffusion by 6-13% in the entire investigated range of filling with aluminosilicate microspheres.

It has to do with the fact, that fine aerosil with a high specific surface ensures the formation of a denser packed structure, partially filling the interspherical space, which is formed by particles of microspheres with a diameter of 10-100 microns, this leads to a decrease in the surface defectiveness of the styrene-acrylic coating.

Localization on the surface of defect structures of particles of hydrophobised aerosil leads to a decrease of wetting defective structures with water, as a result of which the wetting of the surface of the styrene-acrylic coating deteriorates and capillary diffusion decreases.

Analysis of the obtained micrographs confirms that the microspheres form large agglomerates, between which there are free vacancies, which will negatively affect the operational properties of the developed coatings.

At the same time the introduction of aerosil allows to obtain a more ordered structure, which makes it possible to obtain a coating with lower internal stresses, increased aggregate stability and, as a consequence, with improved technological and operational properties.

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